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IDENTIFICATION OF CHEMICALLY-SPECIFIC SITES ON COAL SURFACES

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IDENTIFICATION OF CHEMICALLY-SPECIFIC SITES ON COAL SURFACES

by

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TABLE OF CONTENTS

			Page
Summary			3
Chapter 1	-	Statement of Work	4
Chapter 2	-	Introduction	3
Chapter 3	-	Activation Energies of Coal Oxidation Using SIMS	11
Chapter 4	-	Solvent Swelling and Free Radical Inhibitors	21
Chapter 5	-	Chemical Derivatizations	24
Chapter 6	-	Derivatization Using New Procedures Coupled with Analysis other than SIMS Imaging	35
Chapter 7	-	Conclusions	39
		References	44
		List of Tables	46
		List of Figures	47
		Appendix	48
Tables			
Figures			

SUMMARY

The oxidation of coal has been studied using two surface-sensitive spectroscopic techniques: Secondary Ion Mass Spectrometry (SIMS) and X-ray Photoelectron Spectroscopy (XPS or ESCA). In this study site specific reagents have been used to identify oxygen functional groups on the coal coal surface and thus to elucidate the mechanism of the low-temperature oxidation of coal. SIMS imaging has been especially useful in determining the surface distribution of specific reaction products. XPS was used to confirm that reaction had been achieved prior to SIMS analysis in those instances where isotopically enriched reagents were not used (in the later case only SIMS was effective in identifying reaction products).

A SIMS technique was developed which permits measurement of the activation energy of the low temperature oxidation of coal in individual coal macerals. The results obtained are in good agreement with published values.

The site-specific reagents provide evidence that coal oxidation proceeds by a free radical chain mechanism initiated by surface adsorption of O_2 followed by peroxide formation and cleavage. Consistent evidence suggests that the process is catalyzed by minerals in the coal matrix.

CHAPTER 1

STATEMENT OF WORK

During the past three years the CANMET Energy Research Laboratory has explored analytical methods which can determine the distribution of different inorganic and organic components within certain types of Canadian coals. Much of this work has been done using Secondary Ion Mass Spectrometry (SIMS) in a mode where the spatial distribution of trace and major elements can be determined with micron-scale resolution.

A major long-term goal for this work has been to improve the mechanistic understanding of low temperature oxidation processes in coal (T 100°C). Recent SIMS work has focussed on the measurement of trace oxygen uptake into coal and a determination of its spacial distribution at the oxygen-coal interface. Using SIMS under high mass resolution conditions, the distribution of an ^{18}O tracer can be measured quite unambiguously.

The success with the ^{18}O tracer on reactive coal surfaces has suggested that other ions could also be used as tracers to

react with and identify chemical sites for which they have a unique reactivity. This approach has already been used successfully to identify acidic hydrogen sites on coal surfaces. This was accomplished by Corcoran et al.,[17] using barium as a hydrogen site-specific ion and Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (SEM-SED) to image the Ba distribution. The uptake of barium onto carboxylic acidic sites on coal has also recently been quantified by infrared spectroscopy, using the shift in C=O vibration frequency from 1700 to 1560 cm-1 as the metal was bonded. Preliminary SIMS studies of barium reactions with pyrite in fusinite have shown that barium is strongly bonded as a sulphate to the pyrite surface.

Since SIMS is capable of imaging virtually all elements in a wide concentration range, studies such as Corcoran's could clearly be expanded, and much more detailed information extracted. For example, coal surfaces oxidized in $^{18}O_2$ and reacted with $Ba(OH)_2$ could be analyzed for the distribution of Ba, ^{16}O and ^{18}O. The distribution of Ba would be correlated with acidic hydrogen, the coincidence of Ba and ^{16}O would be indicative of acidic sites present in the coal before ^{18}O oxidation and coincidence of Ba and ^{18}O would constitute evidence for the generation of new acidic H sites.

Successful completion of this phase of the work would precede reactions of greater sophistication. For example,

barium acetate is known to react with carboxylic OH, but not with phenolic OH. Comparison of images obtained by treating the coal surface first with barium acetate and then with barium hydroxide would identify macerals richer in one of these species. The use of more simple bases such as NaOH and KOH in conjunction with $NaHCO_3$ and $KHCO_3$ (the latter will react with phenolic OH) should be possible in coals depleted in Na and K. These species would eliminate the risk of carbonate contamination via reaction of atmospheric CO_2 with $Ba(OH)_2$. The use of $Rb(OH)_2$. The use of Rb(OH) is also attractive, since Rb is rare in coals.

TASK ONE

Construction of equipment which will permit the effective degassing of all solutions and which will provide an inert atmosphere. This will prevent the precipitation of carbonates such as $BaCO_3$ and, by eliminating dissolved oxygen, would suppress oxidation of the coal surface in basic solution.

TASK TWO

The distribution of oxygen and barium on coals oxidized in air at 100°C and 150°C would be determined by SIMS after treatment with $Ba(OH)_2$ and $Ba(CH_3OO)_2$. These studies will be carried out on at least four Canadian coals (two western and two eastern) supplied by the Scientific Authority.

TASK THREE

The studies outlined in task two would be extended to other bases and bicarbonates and to other oxidative systems.

TASK FOUR

In conjunction with tasks 1-3, SEM and XPS studies of the coal surface would be undertaken and analysis of the gases produced during oxidation would be carried out using GIMS, and the residual gas analysis capacity of the SIMS instrument. Should the project be continued beyond a first phase more specific reagents, such as Tollens solution and aqueous bromine could be explored.

CHAPTER 2

INTRODUCTION

Freshly mined coal oxidizes readily in air. This reaction results in autoignition in extreme cases and loss of coking properties in others. The early stages of the oxidation process remain poorly understood largely because the chemical complexity and heterogeneity of the material steadfastly resists standard analytical methods and bulk analyses aimed at discovering subtle changes associated with mild of oxidation. Surface sensitive techniques such as Secondary Ion Mass Spectrometry (SIMS), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) offer the best means of detecting the products of oxidation in its earliest stages at the gas/solid interface.

Our group has prepared three earlier reports[1-3] dealing with the application of these methods to the elucidation of the structure of coal and its attendant inorganic components and the synergism between these features and low temperature oxidation. The first Report (1) describes the use of SIMS imaging to examine details of the structural relationships between inorganic species and individual maceral groups. The second used isotopically-labelled oxygen on a variety of coals and maceral types to measure oxygen uptake as a function of rank, maceral type and temperature. The third Report concentrated on those aspects of coal surface chemistry which might lead to enhanced oxidation. At this stage of the study the distribution

of oxygen functional groups was examined using site-specific derivatization reactions while X-ray Photoelectron Spectroscopy (XPS) was used to follow the oxidation states (chemical environment) of reactive species. This segment of the study has been especially fruitful in that it:

1. Provided an effective means of studying oxygen functional groups on the coal surface (via derivitization).
2. Showed the ^{18}O distributions could be used to estimate the activation energies of oxidation reactions using SIMS image intensities.
3. Showed that derivitization in conjunction with XPS can be used to confirm specific reaction mechanisms - in this case that sulfonation of coal may often result from oxidation of pyrite[4] in the coal matrix.

The present report extends these results in several ways. 1. A method has been devised to determine the activation energies of specific oxidation processes within individual coal macerals using ^{18}O oxidation followed by SIMS analysis. 2. In addition, the range of derivitization reactions at our disposal has been extended to include methylation with CF_3I and reaction with Ti(acac)*. 3. The interpretation of more familiar reaction products, (such as those resulting from the use of Tollen's Reagent) have been extended. 4. XPS has been developed as a sensitive, rapid means of confirming the presence of specific derivitization products on coal surfaces prior to SIMS

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* Titanium (Diisopropoxide) bis (2,4 Pentane dionate)

analysis. 5. Changes in the solvent swelling behavior of coals on oxidation have been studied in relation to the presence of free-radical scavengers. Preliminary results show that oxidation is inhibited by ascorbic acid. We intend to continue these latter studies using ^{18}O, SIMS and XPS.

The Report is divided into four sections: ^{18}O and the study of activation energies; Solvent-swelling and inhibition of oxidation; Chemical derivitization; and Conclusions.

CHAPTER 3

ACTIVATION ENERGIES OF COAL OXIDATION USING SIMS

1. Introduction

Accurate determination of the activation energy for coal oxidation would obviously provide some insight into the mechanism of coal oxidation. Not surprisingly, the literature contains many references to low activation energies obtained for coal oxidation at low temperatures but there is considerable variation among the values reported; in fact a brief survey reveals values from 33 kJ mol^{-1} (5) to 105 kJ mol^{-1}(6). More surprisingly, there are significant differences between E_a values assigned to the same underlying processes. For simple adsorption activation energies from 42 to 139 kJ mol^{-1}(6) are reported. We have sought to adapt SIMS techniques to the measurement of oxidation activation energies, both to gain some insight into the reasons for such diverse values and to use the capacity of SIMS to study individual macerals.

2. Experimental

Samples were cut from selected coals using a diamond saw. The resulting faces were then polished with diamond grit and finished on a silk wheel. Water was used as the sole lubricant throughout. The resulting faces were exposed to $^{18}O_2$ at 0.2 atm for seven days at 25°C, 70°C and 90°C respectively and the relative uptake was measured by SIMS.

The SIMS analysis was undertaken in the specimen Isolation[7] mode which provides effective suppression of molecular secondary ions. This approach, which has been described elsewhere[8], ensures that the secondary ions detected at mass eighteen represent only ^{18}O. The primary ion beam was $^{16}O^-$ at 200 nA.

These oxygen uptake studies provided coal surfaces containing well defined concentrations of ^{18}O. These specimens were subsequently used as starting materials to monitor ^{18}O exchange with air (desorption). We felt that the activation energy for $^{18}O/^{16}O$ exchange reactions (desorption) should provide a direct measure of the E_a for oxygen adsorption. The starting materials were placed in air at 25, 70 and 90°C and the surface ^{18}O was measured by SIMS as before after a suitable time interval.

All measurements used in E_a determinations were obtained from well-defined vitrinite bands. $^{18}O/12$ C ratios were used as a measure of ^{18}O uptake to correct for any coal matrix effects.

In each case the analysis of the SIMS data was complex and proceeded in the following stages:

(i) A SIMS depth profile was run on the sample and the secondary ion yields of $^{16}O^+$, $^{18}O^+$ and C^+ were measured as a function of time (i.e. depth into the sample).

(ii) The resulting graphs were fitted to a straight line and extrapolated to time = 0. The ion yields corresponding to zero time, hence the initial ion yields, were used in all subsequent calculations since they represent the best

estimate of surface concentration. This approach helps to minimize effects which otherwise could be assigned either to primary ion beam damage to the surface or to diffusion controlled processes.

(iii) A correction was applied to the ^{16}O yields to allow for the ^{16}O implanted by the $^{16}O^-$ primary beam used for the analysis.

(iv) The corrected ^{16}O value was used to calculate the contribution to the ^{18}O yield from the natural abundance of ^{18}O from oxides present in the coal prior to the ^{18}O oxidation step.

(v) The $^{18}O/C$ ratio was calculated using values obtained in steps (i-iv) and the resulting ratios obtained at five sites within the same vitrinite band were averaged to produce a $^{18}O/C$ value characteristic of specific oxidation temperature.

(vi) In sulfur-rich or clay-rich coals the sulfur or silicon values at different sites were normalized to a single value and the normalization ratio was applied to the C, ^{18}O and ^{16}O values. This last step was added since the presence of sulfur or clay implied different local mineral concentration. The normalization process insures that we are comparing sites of similar mineral content.

3. Results and Discussion

i) Determination of correction factor for ^{16}O implantation in coal

Initially results were obtained from a piece of $CaCO_3$ which was chosen as a model compound for $^{16}O^-$ implantation because it was rich both in carbon and oxygen. The depth profile obtained using an $^{16}O^-$ primary beam is shown in Figure 1. The ^{16}O, ^{12}C and ^{18}O yields are remarkably constant with time. The secondary ion yields from which an apparent oxygen enrichment of 1.80 was calculated are shown in Table 1.

The correction factor to be used with coal was obtained in a similar manner using a vitrinite band in P-648 coal. The depth profiles appear in Figure 2 with only ^{16}O and ^{18}O yields shown. The total counts leading to an ^{16}O enrichment factor of 2.82 are shown in Table 1. It is not surprising that the enrichment of ^{16}O in coal is greater than that exhibited by $CaCO_3$ since oxygen is at least an order of magnitude more abundant in $CaCO_3$ than in coal and hence the input of isotopically pure ^{16}O from the primary beam has a greater relative effect in coal. The 2.82 enrichment factor was used for all coals studied. In most instances variations from 1.80 $\rightarrow$ 3.88 would have little effect on the E_a values since the contribution of natural ^{18}O is small in any case.

ii) Measurement of E_a for ^{18}O uptake in P-648 coal

Figure 3 shows a depth profile for C, ^{16}O and ^{18}O in P-648 coal exposed to 0.2 Atm $^{18}O_2$ for 7 days at 70°C. A typical set

of results used in estimating $^{18}O/C$ ratios in P-648 coal at 90°C is presented in Table 2. Similar results were obtained for each measurement of ^{18}O uptake but are not reported in the interest of brevity. It is important to note that the five sites on each coal were examined sequentially. There is no trend indicating a reduction in the ^{18}O signal during any set of five measurements indicating that removal of ^{18}O in the SIMS vacuum is not an important process.

Two complete sets of results were obtained at each temperature (that is two sets of five measurements). These results were averaged and a 95% confidence interval was established using a standard t test. Typical results are shown in Table 3 for the uptake of ^{18}O in P-648 coal.

The values obtained at 90° and 70°C show significant overlap; accordingly an activation energy was not calculated using this pair of temperatures. It is probable that the surface reaction at 90° was near completion after the seven-day period and that the 70° sample was almost complete as well. However, an activation energy can be calculated for the 25°/70° pair using the Arrhenius equation, yielding an E_a of 20.75 kJ mol^{-1} (Table 3). This relatively low value suggests that most ^{18}O results from physical adsorption.

iii) Desorption of ^{18}O from P-648 coal

The desorption was carried out by exposing the samples from the ^{18}O uptake experiments to air at three temperatures for a period of one week. The results are shown in Table 4. These

data indicate that desorption had occurred to essentially the same extent in each sample making estimation of an E_a for desorption impossible. About 90% of the ^{18}O is desorbed suggesting that about 10% of the initial uptake results in irreversibly bound oxygen, presumably present in the form of oxygen functional groups. It is interesting that the 90% desorption figure is so consistent but furhter interpretation of this data requires a detailed study of the gaseous products. Certainly there is an intuitive feeling that there should be more ^{18}O present in reaction products such as CO_2 from the samples oxidized at 90°C than those oxidized at 23°C.

iv) Measurement of E_a for ^{18}O uptake in Waynesburgh coal

This coal was oxidized and subsequent SIMS analyses were carried out as described for P-648 coal with one important variation. The coal is rich in sulfur, primarily as iron pyrite, FeS_2, with some elemental sulfur and, especially after exposure to moist air, with iron sulfates. As a result, though SIMS analysis was carried out scrupulously within well-defined vitrinite bands, there was a strong correlation between sulfur and ^{18}O intensities in the SIMS spectra. The ^{18}O values were corrected by normalizing the ^{18}O counts to sulfur yield using the formula:

$$^{18}O \text{ normalized} = {}^{18}O \text{ counts} \times \frac{\text{S counts at reference site}}{\text{S counts}}$$

The resulting activation energies are shown in Table 5. Compared to those reported above for the P-648 coal and those

reported below for P-807) the results show that E_a values increase as the temperature increases. This indicates that more energetic processes dominate at higher temperature. Similar results are reported by Sevenster[9] and by Carpenter and Giddings[10]. This trend is to be expected if low energy processes such as adsorption dominate at low temperature and high energy steps such as formation and/or decomposition of oxygen functional groups become more important.

Our results indeed suggest that at lower temperatures physical and chemical adsorption dominate the process of oxygen consumption. At higher temperatures E_a values are those expected for cleavage of peroxide type bonds[11]. In addition the E_a calculated between 23°C and 90°C must include a number of low energy processes characteristic of the dominant mechanism at 23°C and high energy processes characteristic of the dominant mechanism at 90°C. The E_a value obtained using the two lower (23 and 70) and the two higher (70 and 90) pairs of temperatures are probably more accurate than those obtained from the extremes (25° and 90°).

v) Waynesburg desorption

The P-648 coal showed essentially complete desorption at all temperatures after seven days. The Waynesburg material provided the best sample in the desorption study from which an activation energy could be estimated for the removal of ^{18}O from the sample. The results are shown in Table 6.

Complete desorption was observed at 23°C. Accordingly only the 70°C/90°C data was used to estimate the desorption

activation energy. The high activation energy obtained (90 kJ mol^{-1}) suggests decomposition of oxygen functional groups.

vi) Measurement of E_a for ^{18}O uptake in P-807

The P-807 was treated with ^{18}O and a SIMS analysis of the ^{18}O uptake was measured as for the P-638 coal. The E_a values obtained are reported in Table 5. In this case the highest activation energy is obtained for the pair of $^{18}O/C$ values measured at 23°C and 70°C with the value decreasing for successive pairs involving 90°C. It is likely that surface reactions reached saturation at 90°C prior to completion of the experiment and the value of 74.0 kJ mol^{-1} obtained between 23°C and 70°C is suspect, though it probably represents a lower limit since if reaction at both temperatures was nearing completion the appearent difference in reactivity would be reduced. Thus in this low rank coal the E_a for ^{18}O uptake is relatively high at low temperature. It would appear that oxidation reactions occur at lower temperatures in the lower rank coals. This is probably because the lower rank coals are richer in reactive oxygen functional groups which undergo further oxidation. In the higher rank coal the reactive groups must first be generated, hence two distinct mechanisms exist

I LOW RANK $\rightarrow$ REACTIVE GROUP + O_2 $\rightarrow$ PRODUCTS

II HIGH RANK COAL + O_2 $\rightarrow$ COAL O_2 $\rightarrow$ REACTIVE GROUP + O_2 $\rightarrow$ PRODUCTS

vii) P-807 desorption

The uptake of ^{18}O by P-807 was as expected[12] most marked as was desorption.

In Table 7 results at 70° and 90° show complete reaction as before so that the data is not useful in estimating E_a for ^{18}O removal. The data between 90° and 25°C are clearly suspect due to the similarity of the 70° and 90° results making the value of 91 kJ mol^{-1} obtained between 25° and 70°C the most reliable in the set. If we accept the latter value as a good estimate then it, as that for Waynesburgh, is indicative of a decomposition process.

4. Conclusions

The Waynesburg data is the most reliable and in the best agreement with other authors.[5,6,9,10] There is clear evidence that, as the temperature rises different processes become important. Our data shows at least two different activation energies. We suggest the mechanism is

$$COAL + O_2 \rightarrow COAL\ O_2 \rightarrow \text{Oxygen functional groups} + O_2 \longrightarrow$$

$$\text{Further oxidation} \rightarrow \text{Pyrolysis}$$

The desorption data presents clear evidence for rapid removal of adsorbed oxygen followed by a slower, more energetic oxygen removal. The latter process is probably the result of pyrolysis of reactive oxygen functional groups formed during the initial oxidation.

In the case of the P-807 and P-648 coal reactions the results are difficult to interpret because the oxidation times selected were generally too long and the data suggests reaction was complete before the oxidation period at 90°C was terminated for analysis. Further, the same is almost certainly true of the results at 70°C. Accordingly, for these two coals the conclusions are tentative and the E_a values obtained should be regarded as lower limits.

The results are useful because the evidence they provide is based directly on the occurrence of surface oxygen on the treated coals. They are in good agreement with those of other authors using methods which are not surface sensitive[10] and provide support for models of coal oxidation which postulate adsorption of O_2 followed by peroxide mediated free radical oxidation[6]. These inferences are further supported by direct observation of peroxides on coal using Photoacoustic Infrared Fourier Transform Spectroscopy (PFTIR).[13]

CHAPTER 4

Solvent Swelling and Free Radical Inhibitors

1. Introduction:

The free swelling index of a coal is often used as a measure of oxidative weathering. A related and rapid test is provided by solvent swelling which can be more readily investigated in our laboratory. Since our results and the reports of other authors consistently suggest that oxidative weathering proceeds by a free radical mechanism in which the radicals originate from cleavage of surface peroxides, we wished to study the effect of free radical scavengers on solvent swelling induced by oxidation in selected coals.

2. Experimental:

Each sample was hand ground with a mortar and pestle until the sample could be passed through a Tyler 60 mesh (250 μm) sieve. The resulting material was divided into two batches. One batch was slurried with doubly distilled water, the second with doubly distilled water containing ascorbic acid at a concentration 50 mg/100 mL. Both coal slurries had concentrations of 0.1 g/mL. Air at room temperatures was bubbled through the slurries for five days.

The solvent swelling index was measured at the end of the oxidation period using the method described by Larsen et al.[14] In this approach a finely ground coal sample is placed in a narrow tube and centrifuged, the height of the coal column

is measured and compared to the height obtained after the coal has equilibrated with a suitable solvent. The solvent used throughout was pyridine. In each case five samples were tested and an average result together with a 95% confidence interval was calculated. The results are reported in Table 8.

Additional measurements were carried out on the pH changes in the slurries as a result of their treatment. Since the ascorbic acid yield solutions of pH 3, the pH of the control solutions were adjusted to 3 with HCl and the pH values of the resulting slurries were measured before and after oxidation. Unfortunately the pH was monitored for only two coals. These pH values are reported in Table 9.

2. Results and Discussion

In two of the three coals studied (P-648 and P-807) the solvent swelling index is significantly less for coals slurried with ascorbic acid. In one case no difference is observed (coal P-831). Since elevated solvent swelling is associated with oxidation we conclude that ascorbic acid could be effective in preventing sample oxidation.

The pH changes are more difficult to explain. It is tempting to see oxidation as the sole cause and to suggest that oxidation results in acidic OH groups which lower the pH. Certainly, in the case of P-648 coal this hypothesis fits neatly since the untreated sample changes in pH from 3.0 to 2.5 due presumably to some oxidation of the coal. The ascorbic acid is preferencially oxidized to low molecular weight acid with higher

K_a values (oxalic acid is a good candidate). The coal P-831 is most perplexing, here the untreated coal produces a slurry whose pH goes from 3.5 to 1.7 on oxidation but the ascorbic acid protected sample shows an increase in pH, from 3.5 to 6.0. We have no satisfactory explanation for this result. It is possible that the ascorbic acid was oxidized to CO_2 and hence removed from the solution, or that during oxidation the pH fell to a value which permitted ion exchange reactions to raise the solution pH.

Conclusions

Solvent swelling provides a simple, rapid technique for assessing the effects of various oxidizing conditons on coal. These results constitute strong evidence that free radical scavengers, like ascorbic acid, strongly inhibit coal oxidation. These studies should be pursued further.

CHAPTER 5

Chemical Derivatizations

1. Introduction

A wide variety of site-specific reagents have been used to examine the microstrucuture of coal. Painter[15] has used $Ba(OH)_2$ to change the O-H vibrational frequency of acidic OH groups for study by FTIR. Collier et. al[16] have used Ti(acac) in conjunction with XPS to study OH on glassy carbon electrodes. In addition Corcoran et. al have used $Ba(OH)_2$ as a heavy metal stain in Scanning Electron Microscopic studies of coal[17]. The present authors have used $^{18}O_2$ atmospheres to oxidize coal prior to SIMS analysis[12] and have introduced other site-specific species such as Tollen's reagent (NH_4OH solutions of Ag^+) to identify specific oxygen functional groups in SIMS images[3]. In this chapter we describe:

A. Derivatization followed by SIMS imaging with individual reactants.

B. Derivatization with complementary reactants in sequence.

C. Use of XPS in support of SIMS analysis.

D. Derivatization Using Tollen's Reagent

A. DERIVATIZATION WITH INDIVIDUAL REACTANTS

1. Tollen's Reagent.

Experimental

Fresh coal faces were prepared by cutting larger coal

pieces with a diamond saw followed by polishing with diamond grit and finished on a silk wheel, with water as the sole lubricant. The resulting faces were exposed to Tollen's reagent for ten minutes, washed, air dried and subjected to SIMS imaging.

The SIMS images were obtained with a Cs^+ primary ion beam at 100 nA current with a net accelerating voltage of 7.5 keV. The primary beam was rastered over a 500 μ x 500 μ area and images were obtained from a circular central area 400 μ in diameter.

Results and Discussion

(a) P-807

The results obtained are shown in Figure 4 representing H^-, O^-, OH^-, $C_2H_2^-$, Si^-, O_2^-, $^{107}Ag^-$ and $^{109}Ag^-$. The image at 26^-, $C_2H_2^-$, defines the organic region of the coal and is readily seen to be complementary to the image at mass 28^-,Si^-, which defines the mineral inclusions probably clays. The suite of images at 16^-, 17^- and 32^- representing O^-, OH^- and O_2^- show the organic region of the coal to be extensively oxidized and the OH^- may be taken to be evidence for the presence of acidic hydrogens. The images at 107^- and 109^- are identical and of essentially equal intensity and may thus be confidently assigned to Ag. In addition, the Ag is seen to be confined to the oxidized organic region of the coal and to be moderately enhanced near clay-rich regions.

The observed Ag pattern would be expected if Ag^+ ion were

reduced to metallic Ag by either aldehydes, phenols and/or surface peroxides, all of which are reasonable candidates as surface active oxygen species. The assignment of O_2^- to the image at mass 32^- is made because little sulfur is expected in this coal. In addition no iron was detected (suggesting FeS_2, the most common form of sulfur in coal, is absent from this region) and our previous work using high mass resolution of the mass 32 region has shown O_2^- to be abundant in the secondary ion spectra from heavily oxidized regions of coal. It should also be noted that in this region of the coal no Ag is detected in the mineral-rich regions of the surface.

(b) Waynesburgh Coal

The images obtained from this coal are shown in Figure 5 and represent the distributions of O^-, OH^-, F^-, $C_2H_2^-$, Si^-, O_2^- and S^-, $^{107}Ag^-$ and $^{109}Ag^-$. As in the case of the lignite the $C_2H_2^-$ and Si^- images serve to identify organic and mineral regions, each Si^- image corresponds to an apparant dark area in the organic image. However bright spots associated with F^- do not correspond exclusively either with Si^- or $C_2H_2^-$ regions. In fact the F^- distribution matches that of O^- and OH^-. This could result if F^- replaces for OH^- within the oxidized regions of the coal. The region delineated by O^- and OH^- shows an intimate relationship with the clay regions. The 32^- image probably contains considerable S^- in addition to O_2^- since this FeS_2 is abundant in this coal and some Fe^+ (not shown) is associated with these regions.

The two Ag isotopes provide matched images as before and

provide a rich pattern mainly associated with O^-, OH^- and S. Additional Ag deposits may well be Ag_2S, Ag_2SO_4 and/or Ag_2SO_3, the former being more likely both because of the presence of $S^=$ and because Ag_2S is the least soluble member of the series. Some Ag_2SO_4 and Ag_2SO_3 might also be expected associated with pyrite oxidation.

Although these images are complex and difficult to interpret it is clear that as in the case of P-807 Ag deposition is associated with organic oxygen or sulfur. However intense Ag images are associated with mineral matter which includes iron pyrite. The presence of sulfur thus probably leads to precipitation of Ag_2S with some Ag_2SO_3 and Ag_2SO_4. This experiment suggests that precipitation of insoluble inorganic Ag species occurs on minerals containing suitable anions, in fact in this coal inorganic precipitation may to be the dominant mechanism for Ag deposition.

2. Derivatization using Rb(OH)

(a) Rb(OH) on P-648 Coal

Our early work[3] on coal derivatization used either KOH or $Ba(OH)_2$ in derivatization reactions aimed at imaging coal regions containing acidic OH groups. Results from this investigation were used to draw inferences concerning the production of carboxylic acids during reaction of coal surfaces with Tollen's reagent. These results, while promising, suffered from the disadvantage that K and Ba are common in coal rendering interpretation of results difficult. In addition formation of

hemicarboxylates with $Ba(OH)_2$ was chemically less certain than formation of K carboxylates. This section explored the use of RbOH to identify acidic OH groups. Since Rb is rare in coal and Rb carbonates, being water soluble, do not constitute potential interfering species as with $BaCO_3$. The procedure was similar to that used with Tollen's reagent except that P-648 coal was used and reaction with the base was carried out under a nitrogen atmosphere to prevent formation of Rb_2CO_3.

The results are shown in Figure 6. The images for C^- and O^- show the coal in this region to be largely mineral free and oxidized over the entire area surveyed. The $C_2H_2^-$ shows considerable structure as do the images for the two isotopes of Rb. The reaction of RbOH with the coal surface is clearly specific to certain areas. Identical reaction patterns are obtained for both isotopes. We suggest that RbOH is reacting specifically with acidic OH in coal.

It is interesting to speculate on the differences between the images obtained for H^- and H^+. The H^- is associated primarily with the organic region and is at least two orders of magnitude more intense than the H^+ image. In addition the H^+ image is most intense in regions associated with Rb. It may be that hydrogen bonded directly to oxygen is a better source of H^+ in the secondary ion spectrum. If this is the case then H^+/H^- would provide a valuable direct measure of local oxidation. In addition the C_2H_2 intensity is greatest in regions where no reaction with Rb has occurred.

3. Derivatization (Methylation) with CD_3I

P-648 coal was prepared as before and the surface was methylated with CD_3I using the method of Ettinger et al[18], in which CD_3I is added to a basic, moist tetrahydrofuran in contact with coal. Methyl ethers are formed at OH sites. Methylated regions of the coal were subsequently identified by imaging of D from the surface.

The results are shown in Figures 7 and 8. The coal shown in Figure 7 is divided, as before, into two distinct regions, the organic phase shown by the C^- and $C_2H_2^-$ images and a clay-rich phase shown by the Si^- image. The coal is heavily oxidized as evidenced by the strong O^- and OH^- images. The F^- image is coincident with the OH^- image. The D^- image is well aligned with O^- and OH^- indicating extensive methylation of the coal most probably in the form of methyl ethers but possibly including some acetates. Both the O^-, OH^- and D^- images are general but show enrichment in regions closely associated with clays as defined by the Si^- image.

Figure 8 taken an another location on the coal surface shows a similar pattern with the addition of $28^-(Si^+)$ and $27^+(Al^+)$ images to confirm the presence of alumino-silicate (clay) species. In addition an image was obtained for I^- (127^-)– which was similar to that obtained for $C_4^-(48^-)$. Thus we suggest that some I^- from the CD_3I may have been oxidized to I_2 by peroxides on the coal surface or it may have been adsorbed since I^- adsorption has been reported by Rodriguez et al.[19]

Taken together these two sets of images show that CD_3I may

be used in conjunction with SIMS imaging to identify methylation at organic oxygen sites on coal surfaces.

4. Derivatization with Titanium (Di isopropoxide) bis(2,4 Pentane dionate)*

Collier et al.[14] have used Ti(acac) to react with OH on glassy carbon electrodes. Since this reagent might also be useful in coal derivatization we used their procedure to prepare titanium derivatives of a fresh P-648r coal surface.

The results obtained after derivatization of P-648 coal are shown in Figure 9. The C^-. O^-, Sc^+ and Al^+ images show an organic phase and considerable mineral matter. The oxygen is associated with the areas rich in minerals. Unfortunately the images obtained using positive secondary ions to not give an exact match with the negative secondaries due to slight changes in the ion optics. However the images for Na^+, Al^+, Si^+ and K^+ indicate that alumino-silicates, probably smectite clays, are abundant. The image for O^+ (usually present only if there has been considerable oxidation) is a fair match for the images obtained for three Ti isotopes, 47^+, 48^+ and 49^+. While it is unlikely that a titanium complex has been formed with the mineral matter we feel that a more extensive study of this reaction is required before these images can be interpreted with confidence.

(b) Derivatization With Reactants In Sequence, followed by SIMS Imaging

1. Derivatization of P-648 Coal with CD_3I followed by Treatment with Tollen's Reagent

In this portion of the work the coal was reacted first with CD_3I resulting in methylation at OH sites followed by & Ti(acac) reaction with Tollen's reagent. The ion images are shown in Figure 10.

The images obtained for C (12^+ and 12^-) and for Si(28^+ and 28^-) together with that of oxygen (16^-) show a familiar pattern of oxygen enrichment associated with mineral inclusions. The D^- image, obtained in an unusually long exposure shows methylation in descrete highly localized areas which match the Ag images better than those of any other ion. A good match between the Ag and oxygen images is evident. It is worth recalling that Ag images do not appear to be associated directly with minerals unless sulfides are present (see Figures 4 and 5) and therefore although the underlying reaction sequence is likely to be complex these images may be taken to be indicative of the following reaction sequence.

1. OH groups are methylated by CD_3I. Thus alcohols, phenols and possibly carboxylic acids are capped by this reaction (for what follows the carboxylic acids are irrelevant in any case).

2. Deposition of Ag must now be the result either of reaction with aldehydes or with surface peroxides. The latter is considered to be more likely. Aldehydes could be eliminated if the carboxylic acids which would result from their oxidation by Ag^+ could be shown to be absent. In the next stage we test

this by addition of RbOH to coal treated with CD_3I and Tollen's reagent.

2. Sequential Derivatization of P-648 Coal:

$CD_3I \rightarrow Ag^+ \rightarrow RbOH$

Balmer coal was prepared as before and treated in sequence with CD_3I, Tollen's reagent and RbOH. The results are shown in Figures 11 and 12. In this case, Figures 11 and 12 show three distinct phases: first an organic phase defined by the C^- image and two inorganic regions - an alumino-silicate defined by Si^+ and Al^+ and a calcium-rich region, possibly a calcium apatite outlined by Ca^+. There is a very weak image for D^-. There is a significant I image which closely matches the Ag^+ image obtained at mass 107^-. The positive secondaries however provided an excellent match of 107^+ and 109^+ which, in turn, agreed well with the 40^+ image.

This suite of images is difficult to interpret. The simplest explanation is that a limited number of OH groups are converted to ethers and that Ag is deposited primarily by reduction of Ag^+ by surface oxygen. Some synergistic interaction with the minerals cannot be ruled out but so far there is no evidence for direct Ag deposition on non-sulfide minerals. There is good evidence that formation of apatite in coal is mediated by humic acid complexes of Ca and P[20]. The apparent concentration of Ag in Ca regions may be due to humic substances intimately associated with apatite. This might

explain any concentrations of oxides or peroxides in this region. The F^- image provides further evidence for apatite.

The most important observation is that no Rb image could be obtained. This constitutes evidence that no carboxylic acids were present. We conclude that Ag deposition as a result of surface oxygen (adsorbed or as peroxides) is an important mechanism in this system. There is also a good I image which resembles that of Ag. This may constitute further evidence for peroxide (which could convert I^- to I_2) or adsorption of I^- from the methylation (unreacted methyl iodide is not a possibility because this compound would have hydolyzed during the final stages of the methyl iodide reaction.

Conclusions

This portion of the work shows that a wide range of derivatization reactions on coal are possible and that SIMS imaging provides an ideal means of monitoring the progress of the specific reactions with special reference to macerals and the relationship between local reactivity and mineral matter. We have successfully carried out the following reactions and have obtained reasonably good SIMS images of the products.

1. Methylation with CD_3I (Coal-OH $\rightarrow$ Coal-O-Me)
2. Tollen's reagent (Coal + Reactive Oxygen + $Ag^+ \rightarrow$ Ag)
3. RbOH (Coal Acid $\rightarrow$ Rb Salt + H_2O)
4. Ti acac (Coal-OH + Ti acac $\rightarrow$ Coal-O-Ti)
5. Iodine deposition (Coal-OH + $I^- \rightarrow$ Coal I_2)

The latter reaction (5) will have to be confirmed with

other techniques.

Sequential reaction is especially fruitful. Throughout this work the mechanism of deposition of Ag on the coal surface has been, at once, an interesting experimental result and a perplexing problem because the results were ambiguous since silver deposition would have occurred if Ag^+ were reduced by phenol, aldehydes or peroxides. Reaction of the coal with CD_3I effectively caps the phenols and carboxylic acids. Subsequent reaction with Ag^+ can show Ag deposition only at sites which contain aldehydes or peroxides. If aldehydes are present then Ag^+ reduction should yield carboxylic acids and reaction with RbOH should produce rubidium carboxylates. The P-648 coal subjected to this reaction sequence showed in turn, local deposition of D (from $R-O-CD_3$), well defined regions of Ag and insufficient Rb for imaging. Ag deposition then occurs because of reaction with surface peroxides.

CHAPTER 6

Coal Derivatization Using New Procedures Coupled with Analysis other than SIMS Imaging

1. Introduction

The main body of information in this study has been gathered either from mass spectrometric studies of coals oxidized in $^{18}O_2$ or from SIMS images of derivatized coal. SIMS imaging while yielding the most detailed information is the most time consuming. Accordingly, we have applied XPS, SEM and SIMS bar graph analyses to samples to insure that they are suitable for SIMS imaging, especially after attempting novel derivatizations. This section examines a representative study of results obtained. In addition some of the results which led to our choice of CD_3I, Ag^+ and RbOH for the bulk of this work are presented.

2. Reaction of Coal with Titanium Diisopropoxide bis(2,4-pentanedionate), Ti(acac)

(a) Experimental

Balmer coal was reacted with Ti(acac), using the method described by Collier et al.[16] and the resulting coal surfaces were subjected to SIMS analysis in the specimen isolation mode to verify the presence of titanium. The results are shown in Table 10.

3. Reaction of Coal with $TiCl_2$

$TiCl_2$ is a mild reducing agent. We felt that reaction of coal with $TiCl_2$ might serve as a measure of the oxidizing power of the coal. Accordingly, we attempted reaction with this reagent.

(a) Experimental

P-807 coal was reacted with $TiCl_2$. The resulting surface was subjected to SIMS analysis in the specimen isolation mode.

(b) Results and Discussion

The results confirmed the presence of Ti on the coal surface; however since we were uncertain of the nature of the reaction products we decided to investigate the Ti(acac) system rather than pursue this work.

4. Mehthylation of Coal with CD_3I

Methylatin with isotopically-labed methyl iodide should yield SIMS images corresponding to the OH distribution on the coal surface.

(a) Experimental

Fresh surfaces of P-648 coal were methylated using the method of Ettinger et al[16]. SIMS analysis of the resulting surfaces was carried out in the sample isolation mode.

(b) Results and Discussion

The results giving the ratio of $^2H/^1H$ are shown in Table 11.

5. Treatment of Coal with D_2O

Deuterium exchange between D_2O and acidic hydrogens in coal should provide a rapid indication of the acidity of coal.

(a) Experimental

Fresh surfaces of P-638 coal were dried overnight in vacuum, immersed in D_2O for 10 minutes and dried overnight in vacuum. The resulting surface was analyzed by SIMS in the sample isolation mode.

(b) Results and Discussion

The natural abundance of $^2H/^1H$ is 1.5×10^{-4}. Analysis of the coal at nine random sites yields a value of $1.8 \times 10^{-2} \pm 0.5 \times 10^{-2}$. Although the uptake of deuterium is significant this phase of the work was not pursued, because of ambiguities in the interpretation of the results arising from the difficulty in drying the coal.

5. RbOH and Tollen's Reagent on Coal

These two reagents are treated adequately in the section on imaging although the presence of both species had been confirmed by SEM and XPS; however, the Tollen's XPS obtained for lignite is noteworthy.

(a) Experimental

Ground samples of lignite were exposed to Tollen's reagent for 10 minutes, washed with a rinse of doubly distilled water, dried overnight at 100°C and subjected to XPS analysis.

(b) Results and Discussion

Figure 13 shows an XPS broadscan in which the O 1s, C 1s, Ag $3d_5$ and N 1s peaks are evident. Figure 14 shows the region

from 270 to 299.6 eV. The presence of an oxidized form of carbon, probably a carboxylate, is evident and to be expected since this is a highly oxidized coal. The N may be due to reaction between NH_4OH in the Tollen's solution and the coal. These results help show how XPS and SIMS can be used as complementary techniques when dealing with derivatized samples.

CHAPTER 7

Conclusions

A series of derivatization reactions has been shown to be useful in the study of coal surfaces including reaction between coal and $^{18}O_2$, Tollen's reagent, RbOH, CD_3I and titanium diisopropoxide bi(2,4-pentanedionate). In addition there is evidence that $TiCl_3$, D_2O, NH_4^+ and I^- have some promise for further study.

Reaction of coal with $^{18}O_2$ has already been discussed at length in our previous reports. This study shows conclusively that activation energies for oxygen uptake can be studied using $^{18}O_2$ in conjunction with SIMS analysis. This work has shown that the first step in the oxidation process has a low activation energy ($\sim$ 30 kJ mol^{-1}) and that with increasing temperature higher energy processes dominate ($\sim$ 90 kJ mol^{-1}). In high rank coal the lower activation energy process is more important throughout the temperature ranges studied indicating that most oxygen in these coals is adsorbed. We thus propose two distinct reaction processes depending on rank:

A. High Rank Coals

Coal + O_2 $\rightarrow$ Coal O_2

Coal O_2 $\rightarrow$ Reactive Oxygen Functional Groups

B. Low Rank Coals

Coal Reactive Functional Groups + O_2 $\rightarrow$

Peroxides $\leftarrow$ Hydroperoxides $\rightarrow$ Oxygen Functional Groups

$\longrightarrow$ Thermal Decomposition

Desorption of ^{18}O is seen to be rapid but our data is incomplete. There is strong evidence for a slower process of high E_a (~ 100 kJ mol^{-1}) which is almost certainly due to decomposition of oxygen functional groups on the coal surface.

These results are consistent with previous suggestions for an oxidation mechanism for coal[3,4,7,13]. The stages consist of adsorption of O_2 followed by formation of reactive surface peroxides leading to development of various oxygen functional groups on the coal surface, some of which decompose to yield gaseous products. A particularly good account is given by Lynch et al[11].

Tollen's reagent should deposit metallic silver on the coal surface at sites corresponding to phenols, aldehydes and/or reactive oxygen including O_3 and peroxides. Our work shows consistent, unique patterns of Ag deposition on coal after treatment with Tollen's reagent. These have been observed with SIMS, SEM and XPS. The XPS results often show the presence both of oxidized carbon, possibly carboxylic acids and nitrogen. The latter may be due to reaction of the coal with NH_4^+ to yield either ammonium carboxylates and/or amides.

There is, as yet, no evidence for reaction between Ag^+ and mineral matter in the coal. However, there is a strong suggestion that Ag associated with sulfur-rich regions may be present as Ag_2S or compounds like Ag_2SO_3 or Ag_2SO_4. Our results also suggest that, if apatite formation in coal is mediated by transport of calcium and phosphate by humic substances[20] that the residual carbon would favor Ag deposition on apatite.

Reaction with various titanium compounds has shown promise but study of reactions between coal and $TiCl_3$ have not been pursued because the nature of the products is ambiguous (probably TiO_2 is deposited at reactive oxygen sites). Reaction of Ti(acac) with coal yields distinct Ti images consistent with reaction of the type:

$$\text{Coal-OH} + (\text{i-PrO})_2\,\text{Ti(acac)}_2 \longrightarrow \text{Coal-O-Ti(acac)}_2\,(\text{O-i-Pr})$$

This process has promise for studying OH distributions in coal.

RbOH and D_2O are both good candidates as reagents suitable for identifying labile H in coal. D_2O results are difficult to interpret because of the difficulty in drying the coal before and after reaction. RbOH has proved to be an excellent reagent for identifying acidic sites. It is superior to KOH because K is common in coal and to $Ba(OH)_2$ because Ba is present in coal and formation of hemicarboxylates is a potential problem with Ba^{2+}, as is deposition of $BaCO_3$ resulting from reaction with dissolved CO_2.

Methylation[18] is an accepted technique for preparing derivatized coal. Use of CD_3I adapts the reaction for use as a tool in SIMS analysis since the D provides an ideal isotopic label by which the course of the reaction can be monitored. SIMS imaging of the resulting surfaces has revealed the presence of I on specific areas of the coal surface. The limited results obtained so far are intriguing since they may represent areas where I^- from the methylation process has been oxidized to I_2 by surface peroxides.

Most information from derivatization is obtained from sequential reactions. In this case we have investigated the sequence: Coal + CD_3I → products + Tollen's → products + RbOH → SIMS imaging. In Balmer coal we have found unique distributions of D and rich Ag concentrations, but no Rb after this sequence. The coal has shown significant uptake of all three elements when treated with the reactants individually. The results of sequential treatment can be readily explained by the following sequence:

1. Methyl iodide caps all OH groups.
2. Ag^+ oxidizes any surviving phenols, aldehydes or peroxides - only oxidation of peroxides will not result in new acidic sites.
3. Failure of RbOH shows no acidic sites formed in reaction of Ag^+. In this coal (P-648) Ag^+ must react almost exclusively with surface peroxides. Once again this provides evidence for an oxidation sequence in which surface peroxide formation is an intermediate step.

Finally the solvent swelling experiments indicate that ascorbic acid may be effective in reducing coal oxidation. This observation is also consistent with peroxide formation.

These results represent a major step forward in our study of coal oxidation and provide a direct means of observing organic functional groups on coal surfaces and their distribution relative to different maceral types and to inorganic material present in the coal. The work should now be expanded to include:

1. A more detailed study of peroxide reactions in coal. These results should be repeated after oxidation with H_2O_2.
2. Interferences should be examined, for instance does NH_4^+ form ammonium carboxylates, does I^- react with surface peroxides etc.
3. The reactions examined so far should be used on a wide range of coals and maceral types.

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Table 1 Calculation of ^{16}O enrichment in coal by ^{16}O primary ion beam.

Table 2 SIMS measurement of ^{18}O uptake after exposure of Balmer coal to $^{18}O_2$ at 0.2 atm for 7 days at 90°C.

Table 3 ^{18}O yield from P-638 coal exposed to $^{18}O_2$ at 0.2 atm for 7 days.

Table 4 Desorption of ^{18}O from P-638 coal.

Table 5 Summary of activation energies for ^{18}O uptake in three coals.

Table 6 Rate of ^{18}O desorption from Waynesburgh coal.

Table 7 Rate of ^{18}O desorption from P-807 coal.

Table 8 Solvent swelling for three coals.

Table 9 pH changes in coal slurries during oxidation.

Table 10 Ti isotope abundances in coal treated with Ti(acac).

Table 11 $^{2}H/^{1}H$ ratios for three spots on coal methylated with CD_3I.

LIST OF FIGURES

Figure 1: SIMS Depth Profile for Mass 12, 16 and 18 Daltons in $CaCO_3$.

Figure 2: SIMS Depth Profile for Mass 16 and 18 Daltons in Reference Coal. (P-648

Figure 3: SIMS Depth Profile for Mass 12, 16 and 18 Daltons in P-648 Coal Exposed to 0.5 atm. $^{18}O_2$ at 70°C for Seven Days.

Figure 4: P-807 Coal Exposed to Tollen's Reagent.

Figure 5: Waynesburgh Coal Exposed to Tollen's Reagent.

Figure 6: Waynesburgh Coal Exposed to RbOH.

Figure 7: P-648 Coal After Reaction with CD_3I.

Figure 8: P-648 Coal After Reaction with CD_3I.

Figure 9: P-648 Coal After Reaction with Ti(acac).

Figure 10: P-648 Coal After Reaction with CD_3I followed by Tollens' Reagent.

Figure 11: Negative Secondary Ion Images from P-648 Coal treated sequentially with CD_3I, Ag^+ and KbOH.

Figure 12: Positive Secondary Ion Images from P-648 Coal treated sequentially with CD_3I, Ag^+ and RbOH.

Figure 13: XPS Broadscan of P-807 Treated With Tollen's Reagent.

Figure 14: XPS Broadscan of ClS Region of P-807 Treated with Tollen's Reagent.

APPENDIX.

Descriptions of Coal Used In This Study.

Coal	Moisture	Ash	Volatile Matter	% Elemental Composition C	H	N	S
P-648	0.4	4.5	23.7	84.8	4.6	1.1	0.3
P-831	10.13	11.9	31.4	57.6	3.3	0.8	0.1
P-807	6.3	7.8	32.3	72.1	4.5	1.3	3.8
Waynesburg	2.0	18.7	34.1	63.4	4.7	1.1	2.1
Coleman							

TABLE I

Sample	Total Counts		Expected ^{16}O Counts	^{16}O Enrichment
	^{16}O	^{18}O	(^{18}O counts + 489)	
$CaCO_3$	1.05×10^7	1.19×10^4	5.82×10^6	1.80
Coal (P-648)	1.85×10^5	1.34×10^2	6.55×10^4	2.82

Calculation of ^{16}O enrichment in coal by an ^{16}O primary ion beam.

TABLE 2

Site	Time of Measurement (Seconds)	Counts ^{12}C	Detected ^{16}O	^{18}O	^{18}O Corrected	$^{18}O/C$
1	0	4.3×10^4	2.0×10^3	71.2	69.7	1.6×10^{-3}
	60	4.5×10^4	1.8×10^3	58.2		
	120	4.7×10^4	1.6×10^3	45.2		
2	0	5.0×10^4	3.1×10^3	90.3	88.0	1.8×10^{-3}
	60	5.1×10^4	3.1×10^3	84.8		
	120	5.2×10^4	3.1×10^3	79.3		
3	0	3.4×10^4	1.2×10^3	27.9	27.0	7.8×10^{-4}
	60	3.4×10^4	1.1×10^3	21.9		
	120	3.3×10^4	1.0×10^3	15.9		
4	0	2.8×10^4	2.3×10^3	76.6	75.0	2.7×10^{-3}
	60	3.0×10^4	2.4×10^3	71.0		
	120	3.2×10^4	2.5×10^3	65.4		
5	0	2.7×10^4	1.0×10^3	23.1	22.4	8.4×10^{-4}
	60	2.6×10^4	1.0×10^3	20.1		
	120	2.5×10^4	0.9×10^3	17.1		

SIMS measurement of ^{18}O uptake after exposure of P-648 coal to $^{18}O_2$ 0.2 atm for 7 days at 90°C.

TABLE 3

T	$^{18}O/C$	95% Confidence Interval
90°C	1.255×10^{-3}	$9.189 \times 10^{-4} \rightarrow 1.59 \times 10^{-3}$
70°C	1.072×10^{-3}	$1.07 \times 10^{-3} \rightarrow 1.42 \times 10^{-3}$
25°C	3.57×10^{-4}	$2.52 \times 10^{-4} \rightarrow 4.62 \times 10^{-4}$
		E_a 25°/70° = 20.75 kJ mol^{-1}

^{18}O yield from P-648 coal exposed to $^{18}O_2$ at .2 atm for seven days.

TABLE 4

Initial Uptake Temperature	Desorption Temperature	$^{18}O/C$ Before Desorption	$^{18}O/C$ After Desorption	Diff	% Desorbed
25°C	90°C	1.1×10^{-4}	3.3×10^{-5}	7.9×10^{-5}	70
25°C	70°C	4.2×10^{-4}	5.2×10^{-5}	3.7×10^{-4}	88
25°C	23°C	5.4×10^{-4}	1.4×10^{-4}	4.1×10^{-4}	80
70°C	90°C	1.8×10^{-4}	1.8×10^{-5}	1.6×10^{-4}	90
70°C	70°C	1.7×10^{-3}	1.2×10^{-4}	1.6×10^{-3}	93
70°C	23°C	2.5×10^{-3}	1.9×10^{-4}	2.3×10^{-3}	92
90°C	90°C	1.6×10^{-3}	6.0×10^{-5}	1.5×10^{-3}	96
90°C	70°C	5.3×10^{-4}	5.8×10^{-5}	4.7×10^{-4}	89
90°C	23°C	1.7×10^{-3}	1.7×10^{-4}	1.5×10^{-3}	90

Desorption of ^{18}O from P-648 coal.

TABLE 5

Coal	Temperatures Used °C	E_a/kJ mol^{-1}
P-648	23°/70°	20.8
Waynesburgh	23°/70°	47.1
	23°/90°	56.4
	70°/90°	82.0
P-807	23°/70°	74.0
	23°/90°	53.3
	70°/90°	-3.0

Summary of activation energies for ^{18}O uptake in three coals.

TABLE 6

Temp	$^{18}O/c$ initial	$^{18}O/C$ final	Diff.
23°C	2.3×10^{-7}	2.3×10^{-7}	0
70°C	2.8×10^{-6}	4.6×10^{-7}	2.3×10^{-6}
90°C	1.4×10^{-5}	3.2×10^{-7}	1.3×10^{-5}

E_a based on 70/90 = 90.18 kJ mol^{-1}

Rate of ^{18}O desorption from Waynesburgh Coal

TABLE 7

P-807

T	$^{18}O/C$ before	$^{18}O/C$ after	Diff
25°C	9.9×10^{-5}	6.0×10^{-5}	3.9×10^{-5}
70°C	5.0×10^{-3}	3.0×10^{-4}	4.8×10^{-3}
90°C	4.7×10^{-3}	3.0×10^{-4}	4.4×10^{-3}

E_a 25/70 = 91.1 kJ mol^{-1}

90/25 = 65.2 kJ mol^{-1}

90/70 = -5.9 kJ mol^{-1}

Rate of desorption of ^{18}O from P-807

TABLE 8

Coal	Treatment	Solvent Swelling	95% Confidence
P-648	Air in H_2O	1.29	1.23 - 1.34
" "	Air in H_2O + Ascorbic acid	1.16	1.21 - 1.11
Coleman	Air in H_2O	1.30	1.24 - 1.36
"	Air in H_2O + Ascorbic acid	1.19	1.22 - 1.16
P-831	Air in H_2O	1.70	No Difference
	Air in H_2O + Ascorbic acid	1.70	

(P-807, dissolved in pyridine, no result obtained)

TABLE 9

Coal	Slurrey	pH Before Oxidation	pH After Oxidation
P862	H_2O	3.0	2.5
"	H_2O + Ascorbic acid	3.0	1.8
P-831	H_2O	3.5	1.7
	H_2O + Ascorbic acid	3.5	6.0

pH changes in coal slurries during oxidation

TABLE 10

Mass	46	47	48	49	50
Natural Abundance	7.9	7.2	7.4	5.5	5.3
Detected Trial 1	10.8	7.9	7.2	4.9	4.4
Detected Trial 2	9.9	8.7	7.2	5.2	4.6
Detected Trial 3	10.4	8.3	7.2	4.9	4.4

Ti isotopes in coal treated with Ti(acac)

TABLE 11

NATURAL ABUNDANCE	SPOT 1	SPOT 2	SPOT 3
1.5×10^{-4}	3.0×10^{-2}	6.5×10^{-2}	7.5×10^{-2}

$^{2}H/^{1}H$ ratios for three spots on coal methylated with CD_3I

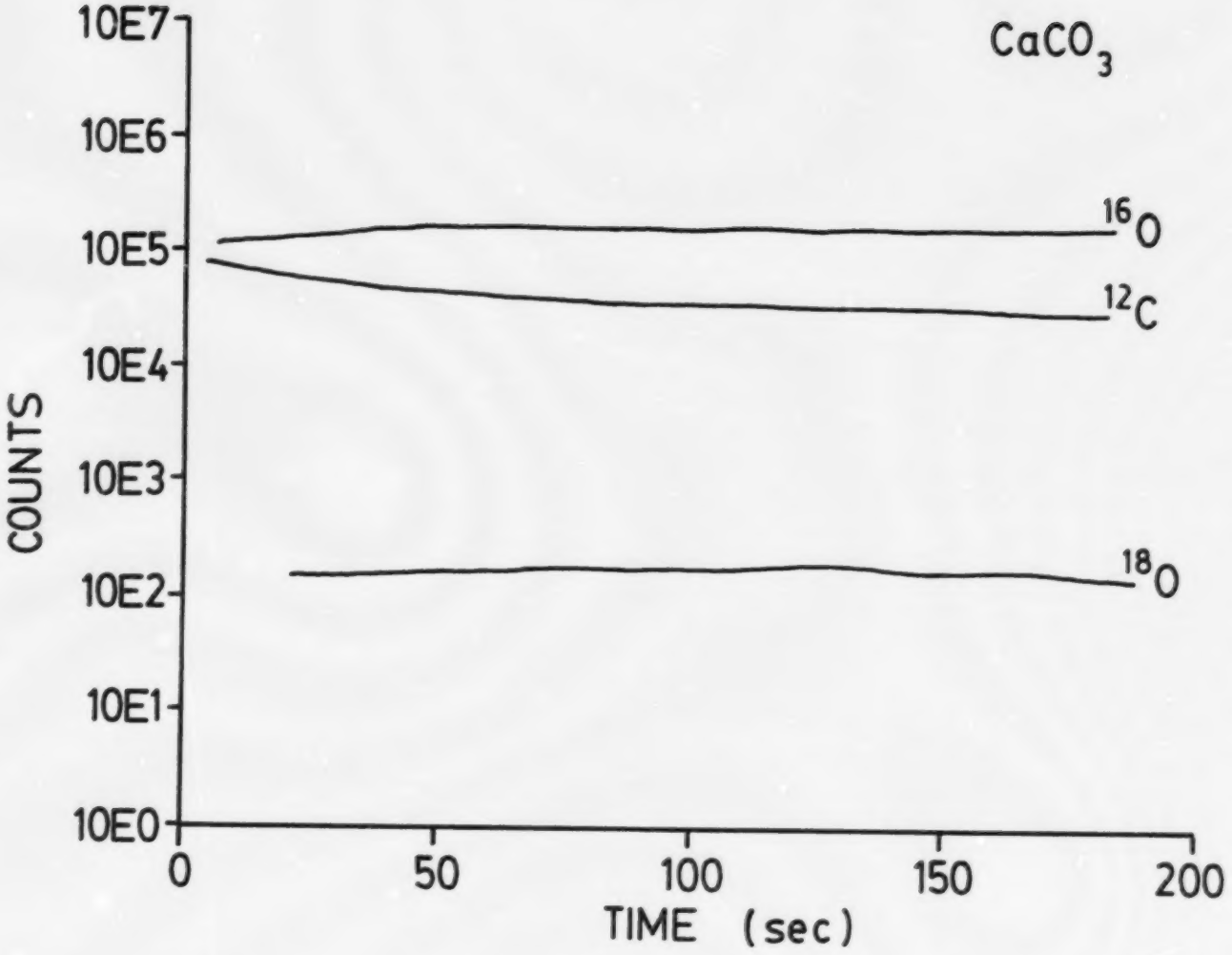


Figure 1
SIMS Depth Profile for Mass 12,16 and 18 Daltons in $CaCO_3$

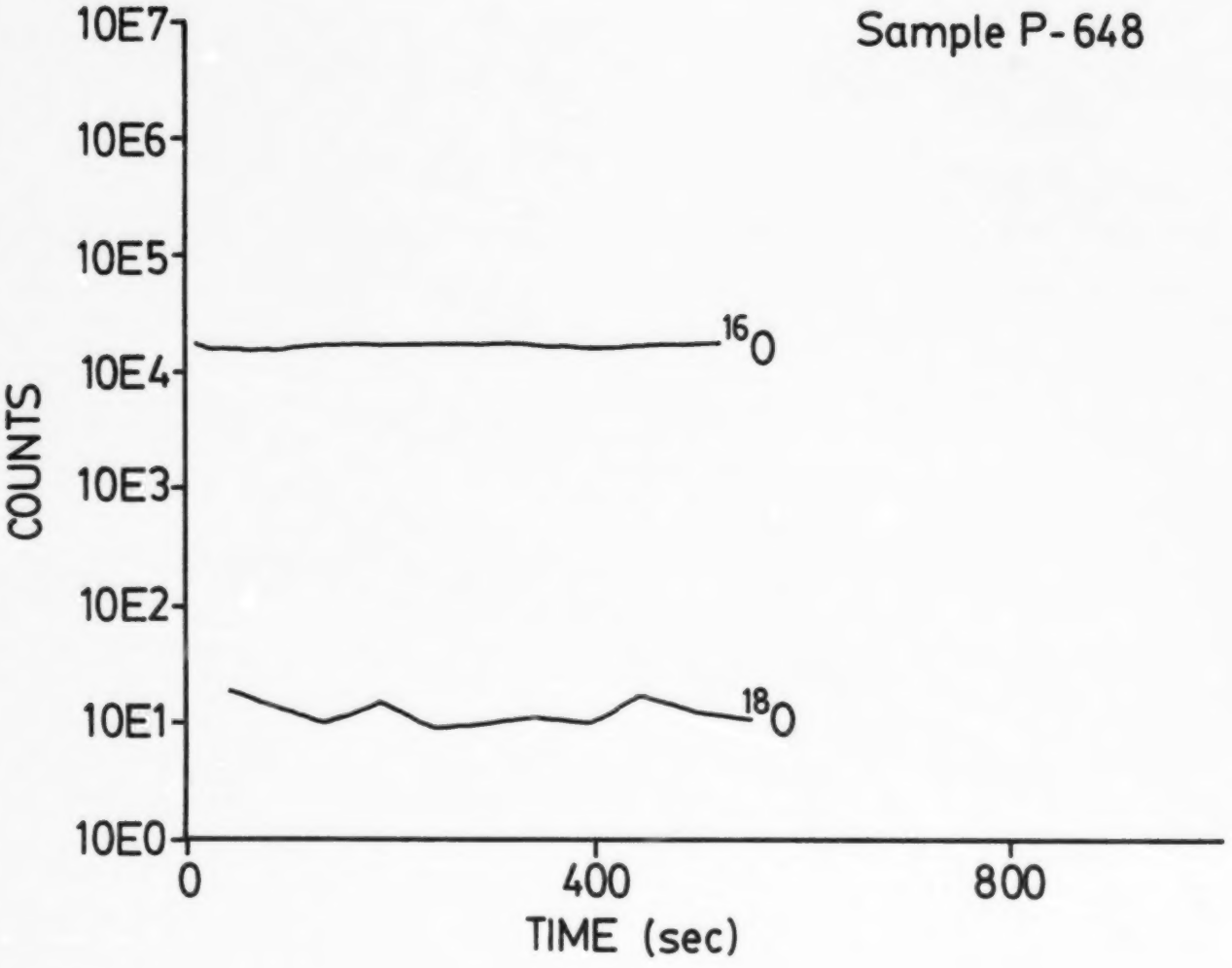


Figure 2

SIMS Depth Profile for Mass 16 and 18 Daltons in Reference Coal.

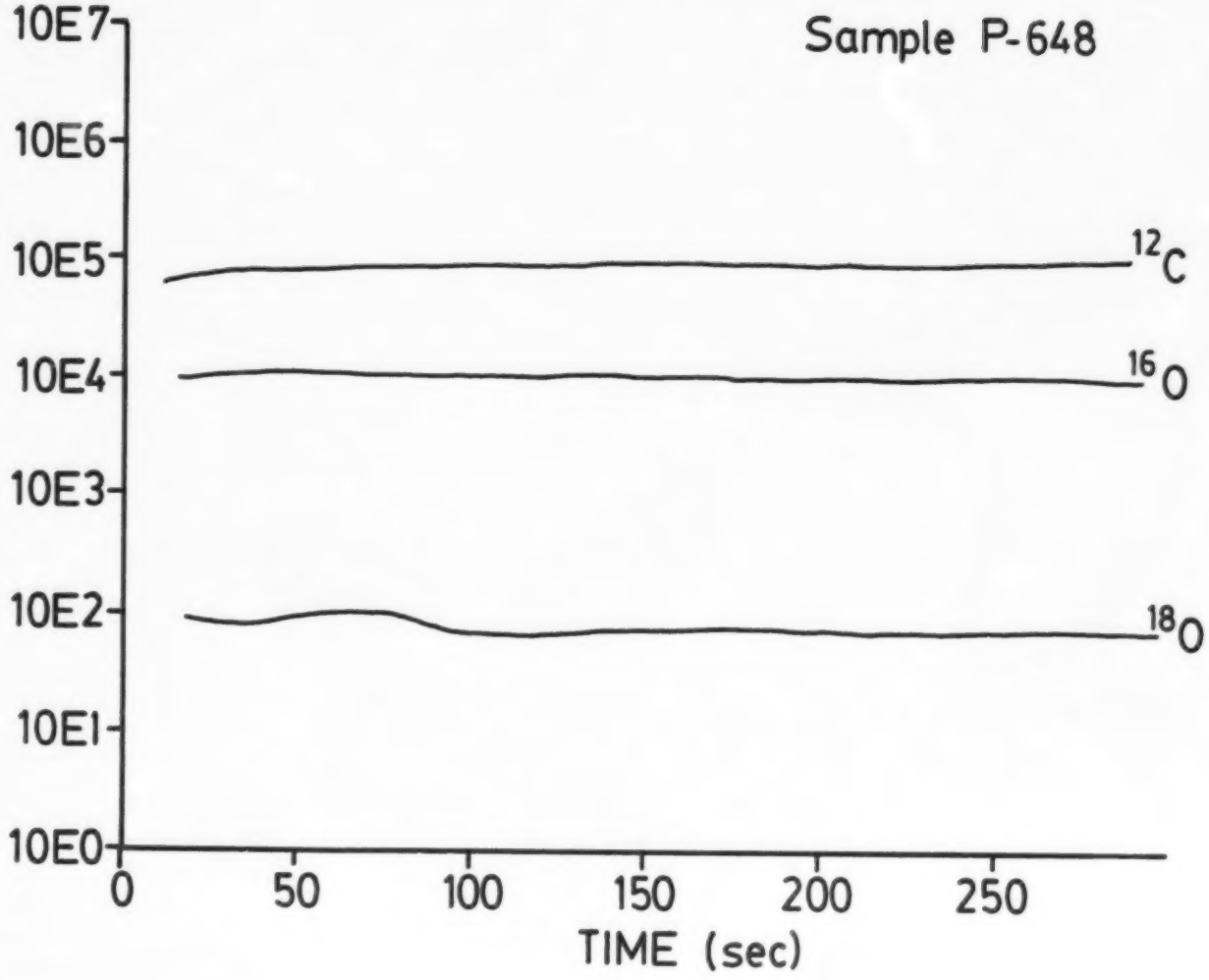


Figure 3

SIMS Depth Profile for Mass 12, 16 and 18 Daltons in P-648 Coal Exposed to 0.5 Atm. $^{18}O_2$ AT 70°C For Seven Days.

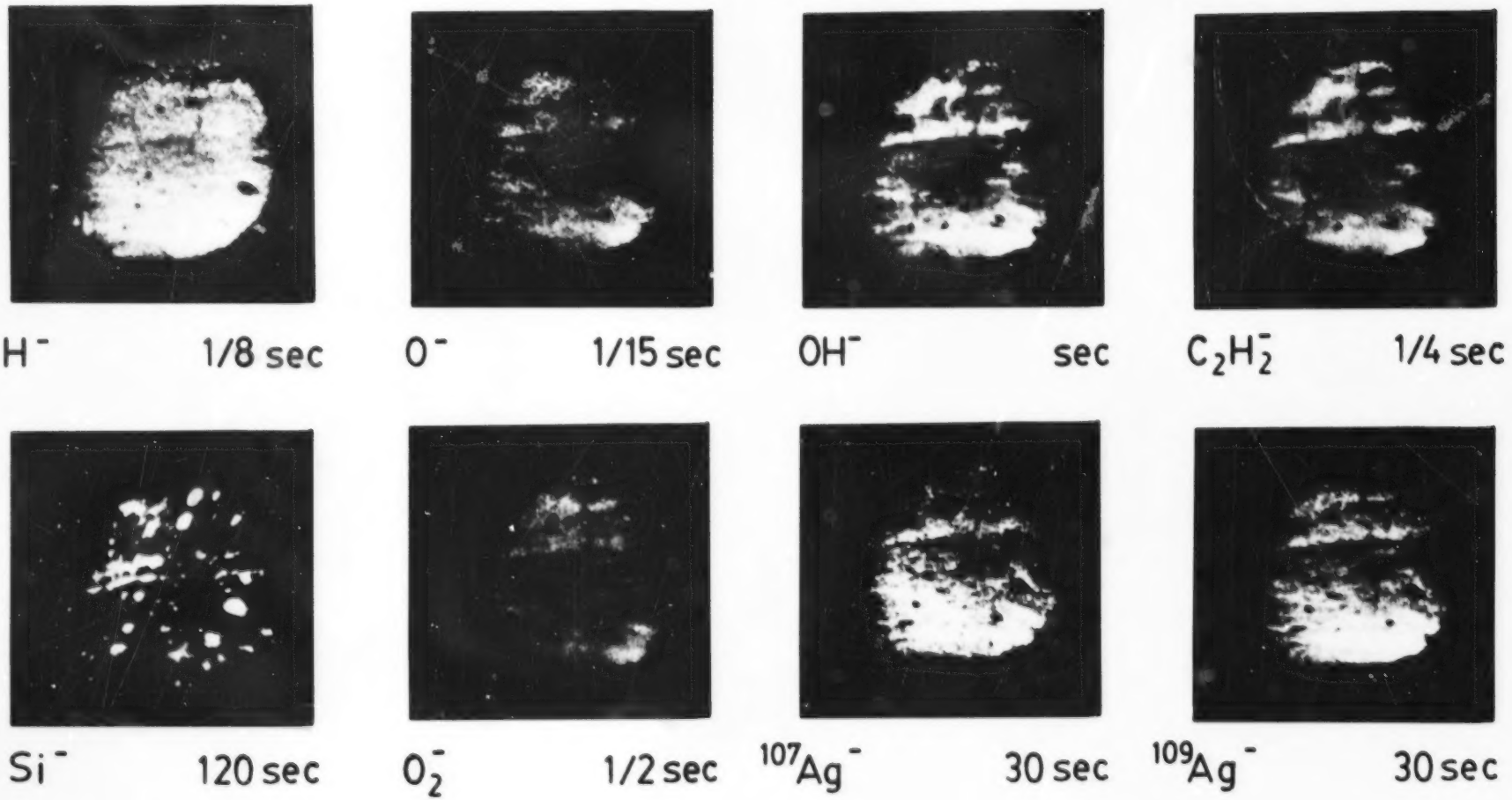


Figure 4

P-807 COAL EXPOSED TO TOLLEN'S REAGENT
IMAGES HAVE A DIAMETER OF 400 μ . EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE

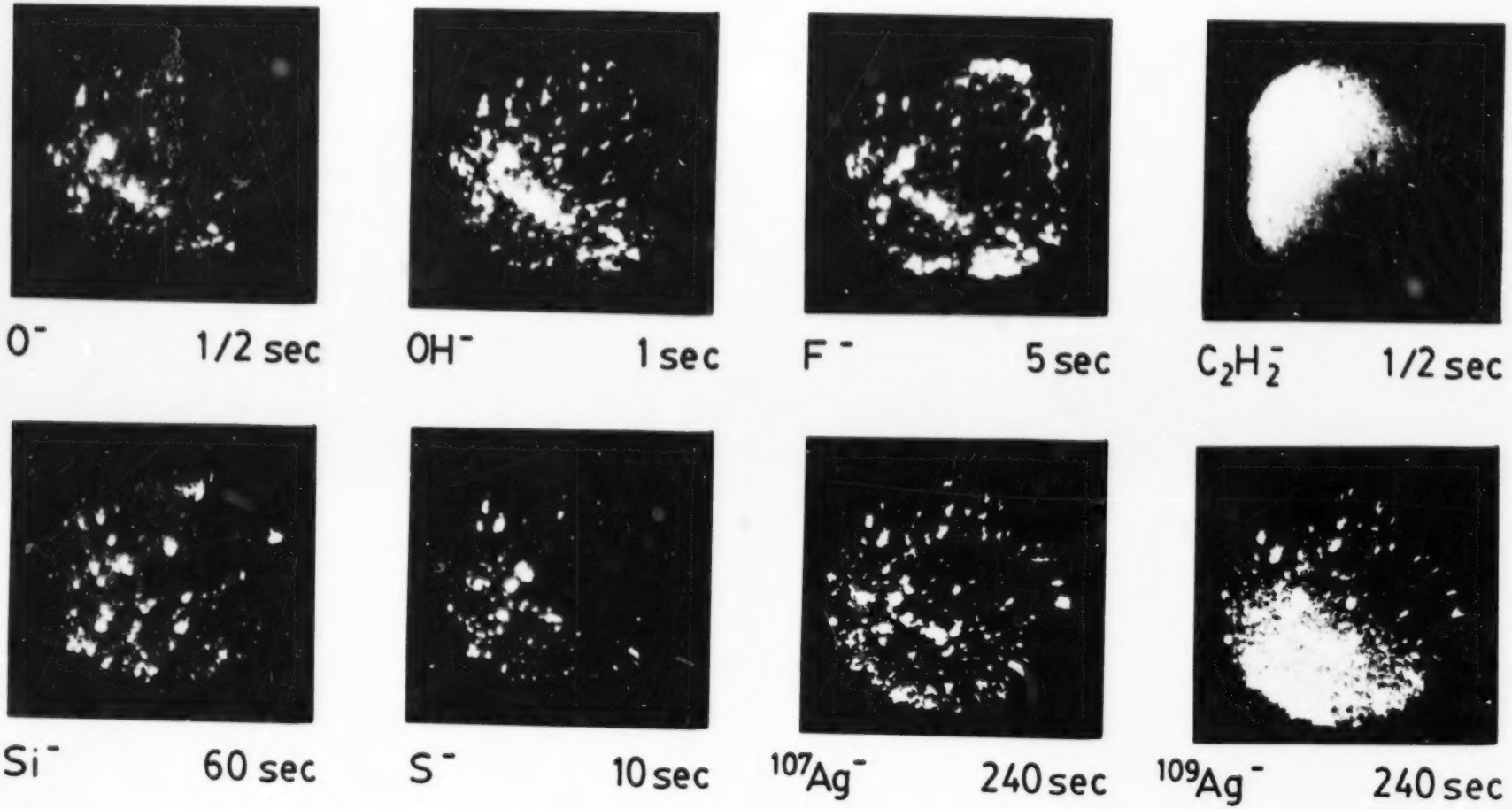
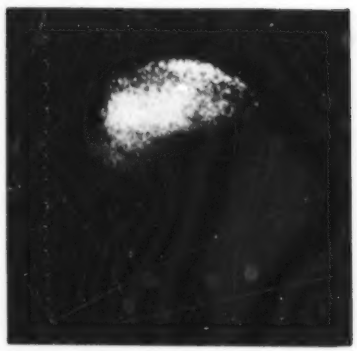


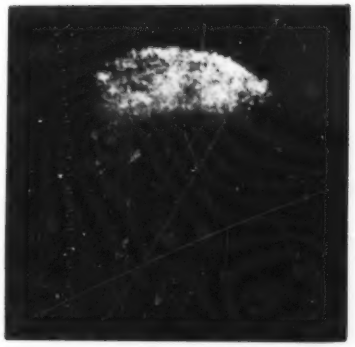
Figure 5

WAYNESBURGH COAL EXPOSED TO TOLLEN'S REAGENT
IMAGE DIAMETER IS 400 μ, EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE

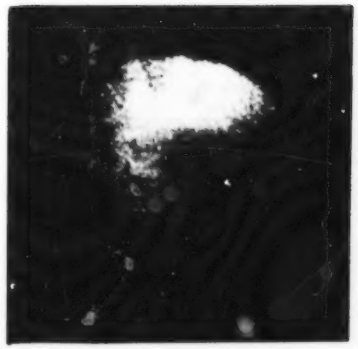


H^- 1/4 sec

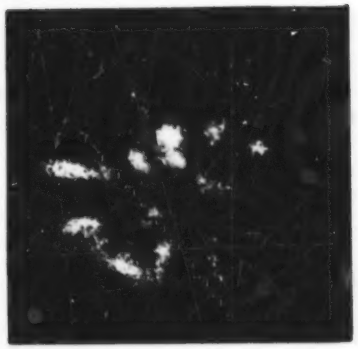
H^+ 60 sec



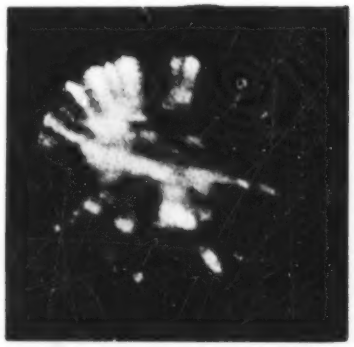
C^- 1/4 sec



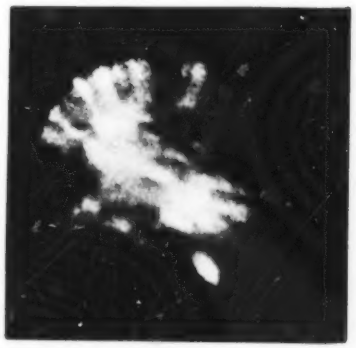
O^- 1/8 sec



C_2H_2 16 sec



^{85}Rb 2 sec



^{87}Rb 4 sec

Figure 6

WAYNESBURG COAL EXPOSED TO RbOH
IMAGE DIAMETER IS 400 μ, EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE

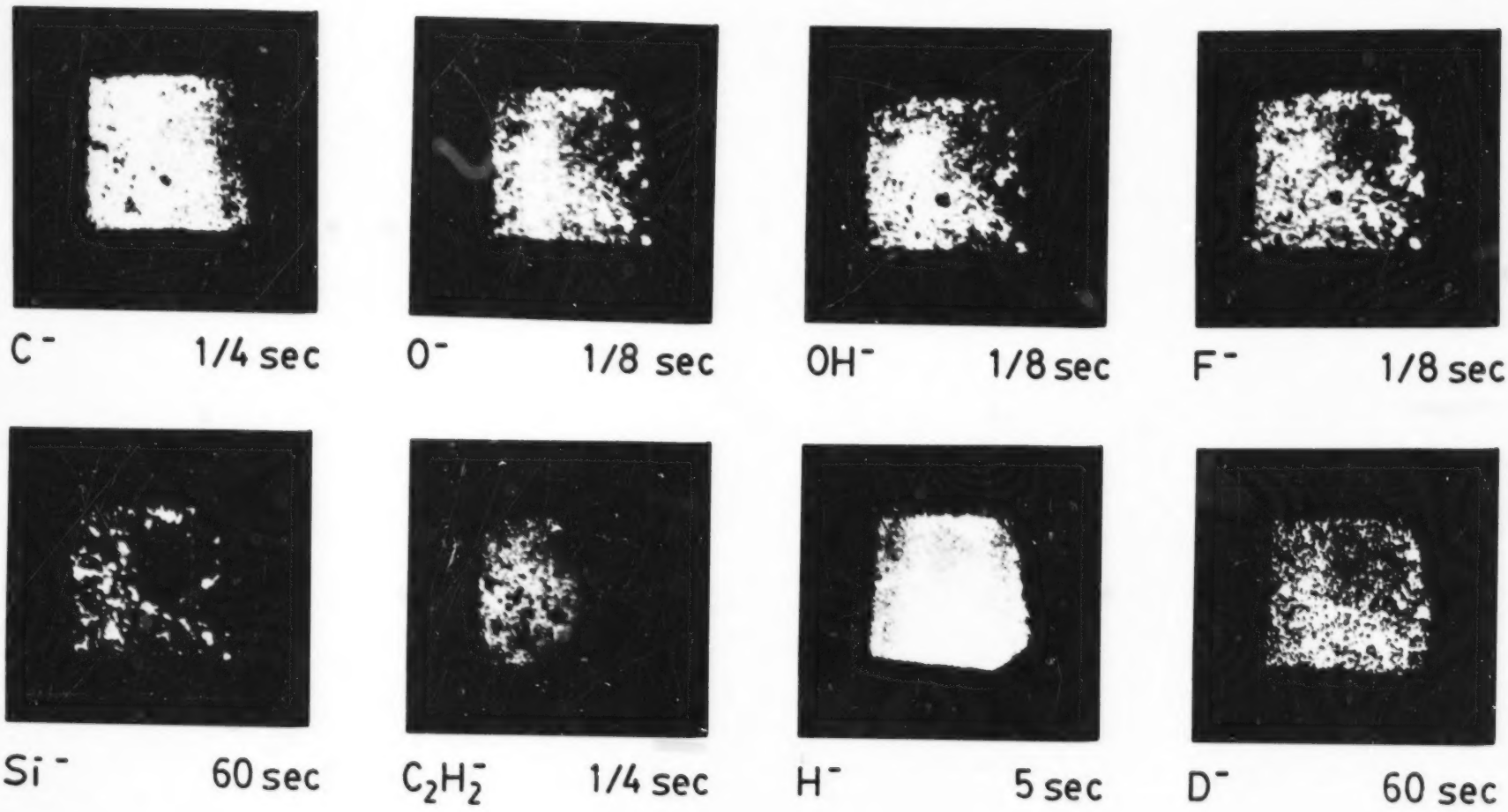
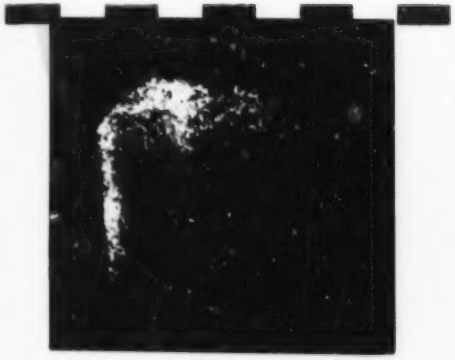
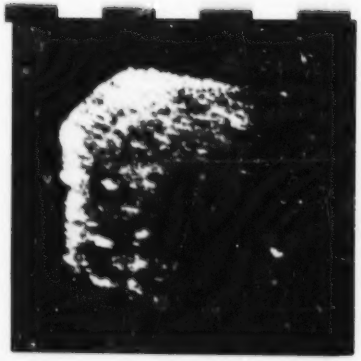


Figure 7

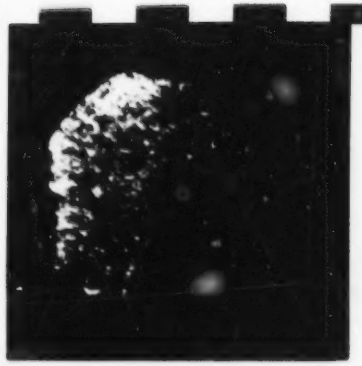
P-648 COAL AFTER REACTION WITH CD_3I
IMAGE FIELD IS 400 μ, EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE



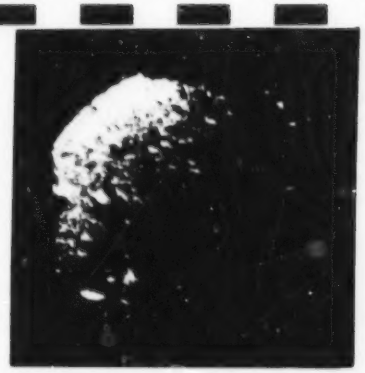
C^- 1/2 sec



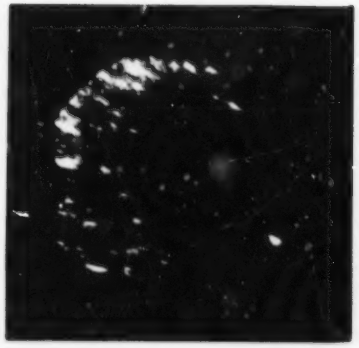
O^- 1/4 sec



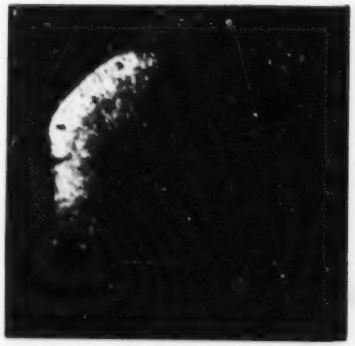
OH^- 1/4 sec



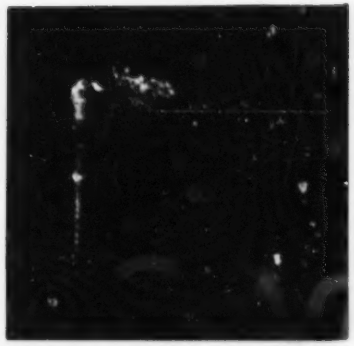
F^- 1/4 sec



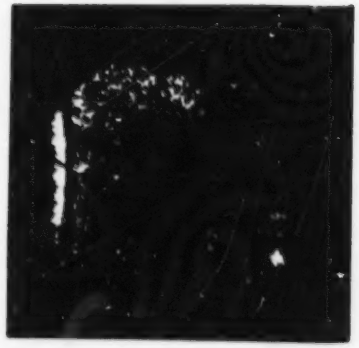
Si^- 240 sec



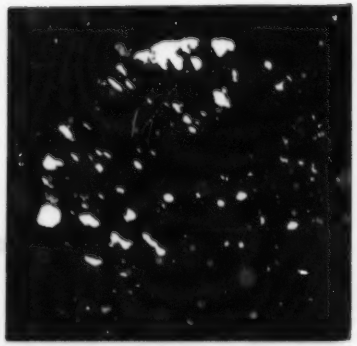
$C_2H_2^-$ 1/4 sec



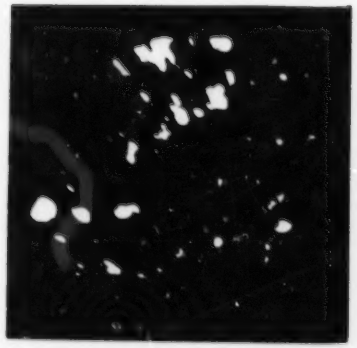
H^- 30 sec



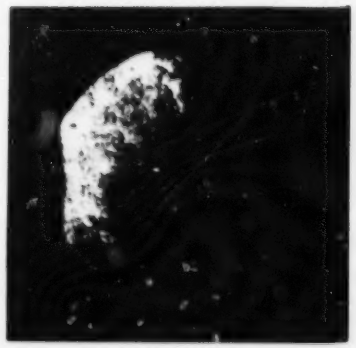
D^- 120 sec



Si^+ 50 sec



Al^+ 30 sec



I^- 2 sec

Figure 8
P-648 COAL
AFTER REACTION
WITH CD_3I
IMAGE FIELD IS 400 μ
EXPOSURE TIMES
ARE RECORDED WITH
EACH IMAGE

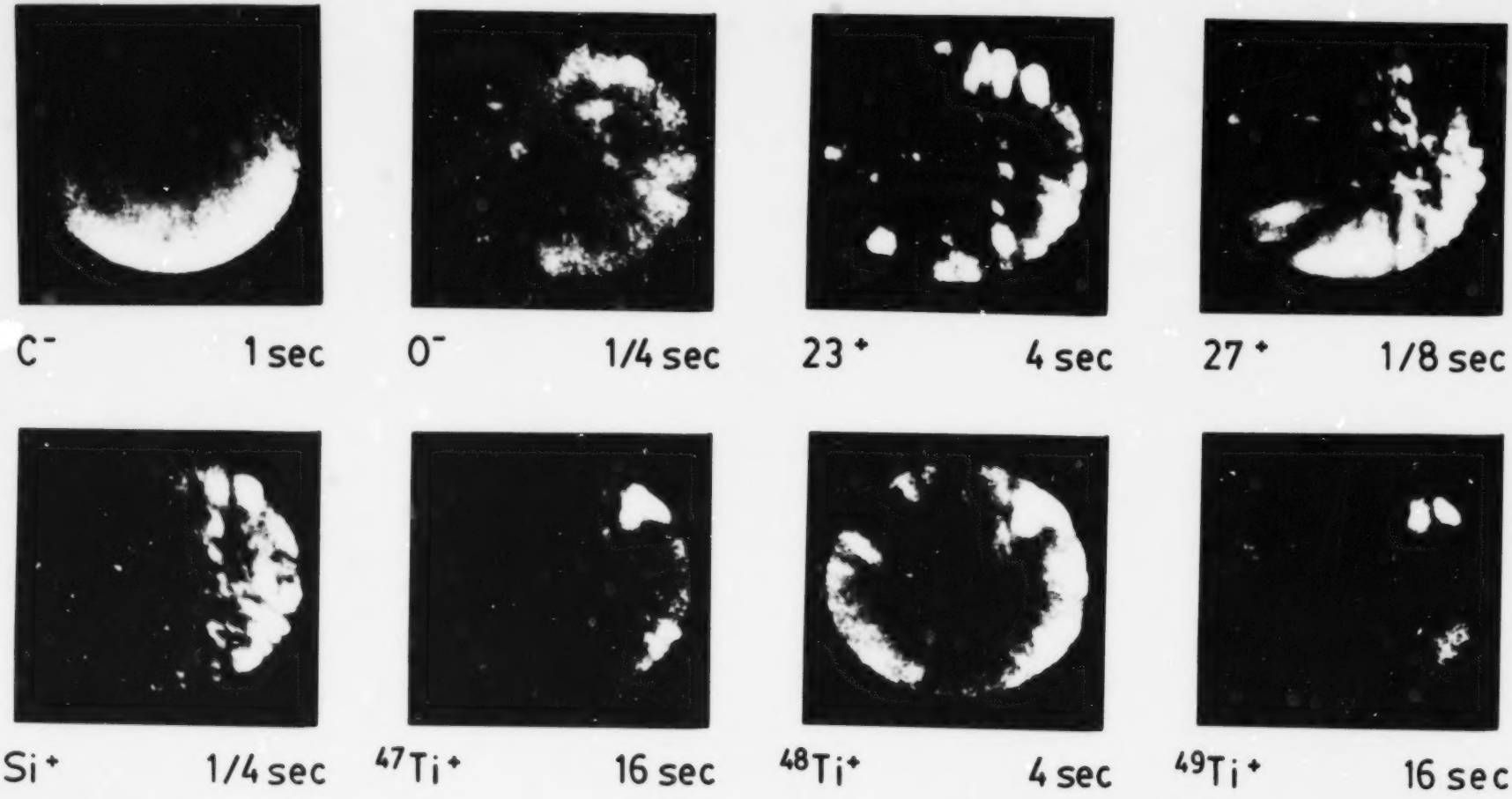


Figure 9

P-648 COAL AFTER REACTION WITH TITANIUM (DIISOPROPOXIDE)BIS (2,4-PENTANEDIONATE). IMAGE DIAMETER IS 400 μ, EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE.

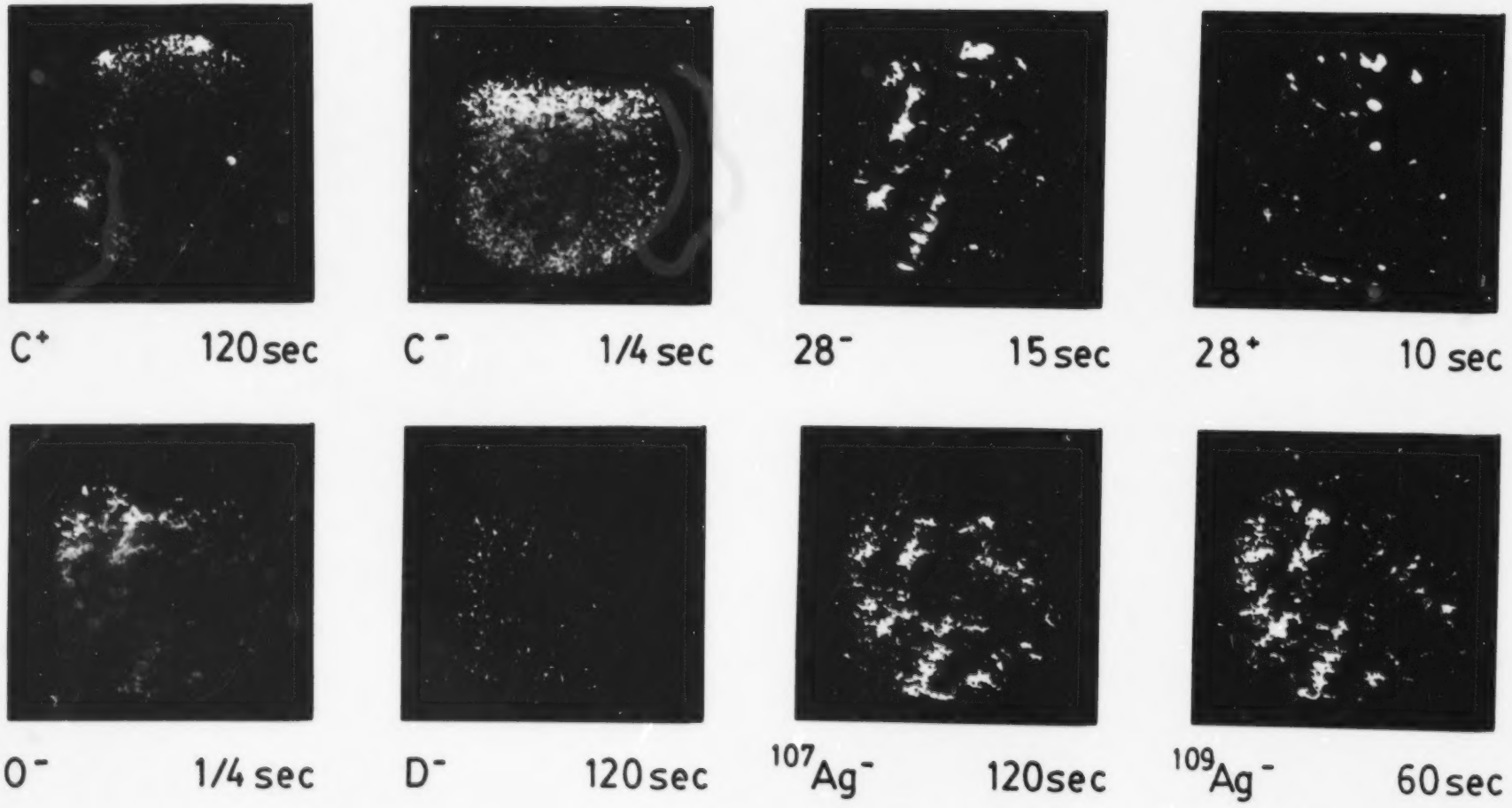


Figure 10

P-648 COAL TREATED WITH CD_3I FOLLOWED BY TOLLEN'S REAGENT IMAGE DIAMETER IS 400 μ . EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE

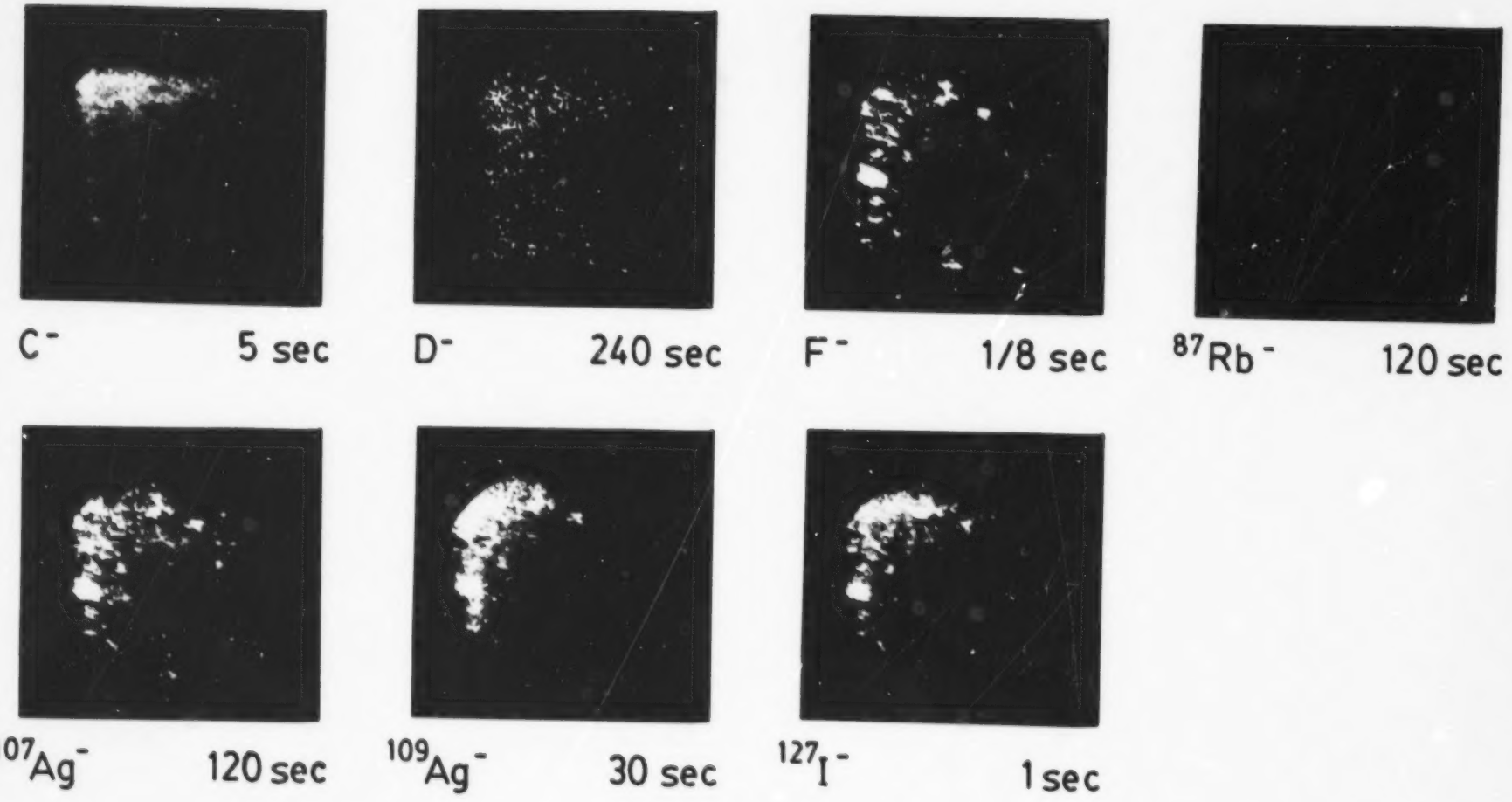


Figure 11

NEGATIVE SECONDARY ION IMAGES FROM P-648 COAL TREATED SEQUENTIALLY WITH CD_3I , Ag^+ AND RbOH
IMAGE DIAMETER IS 400μ , EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE

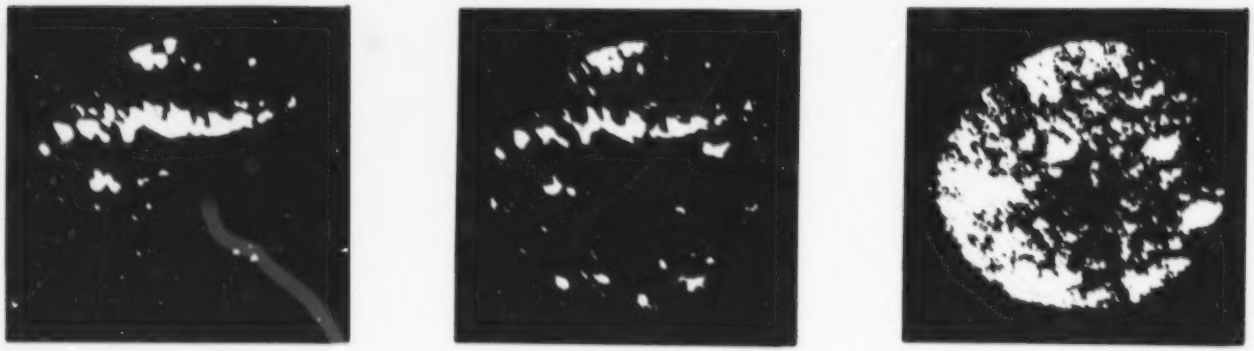
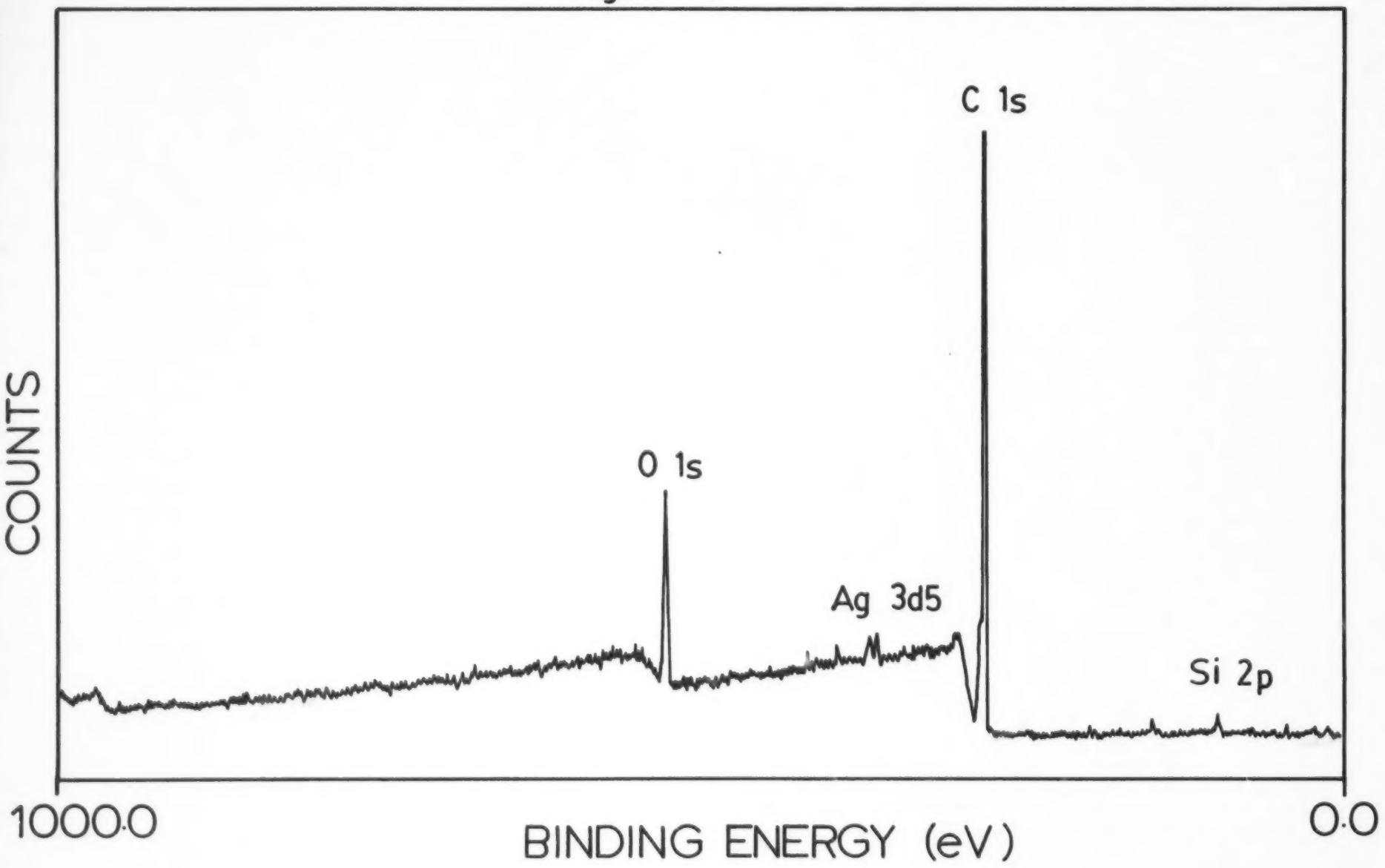


Figure 12

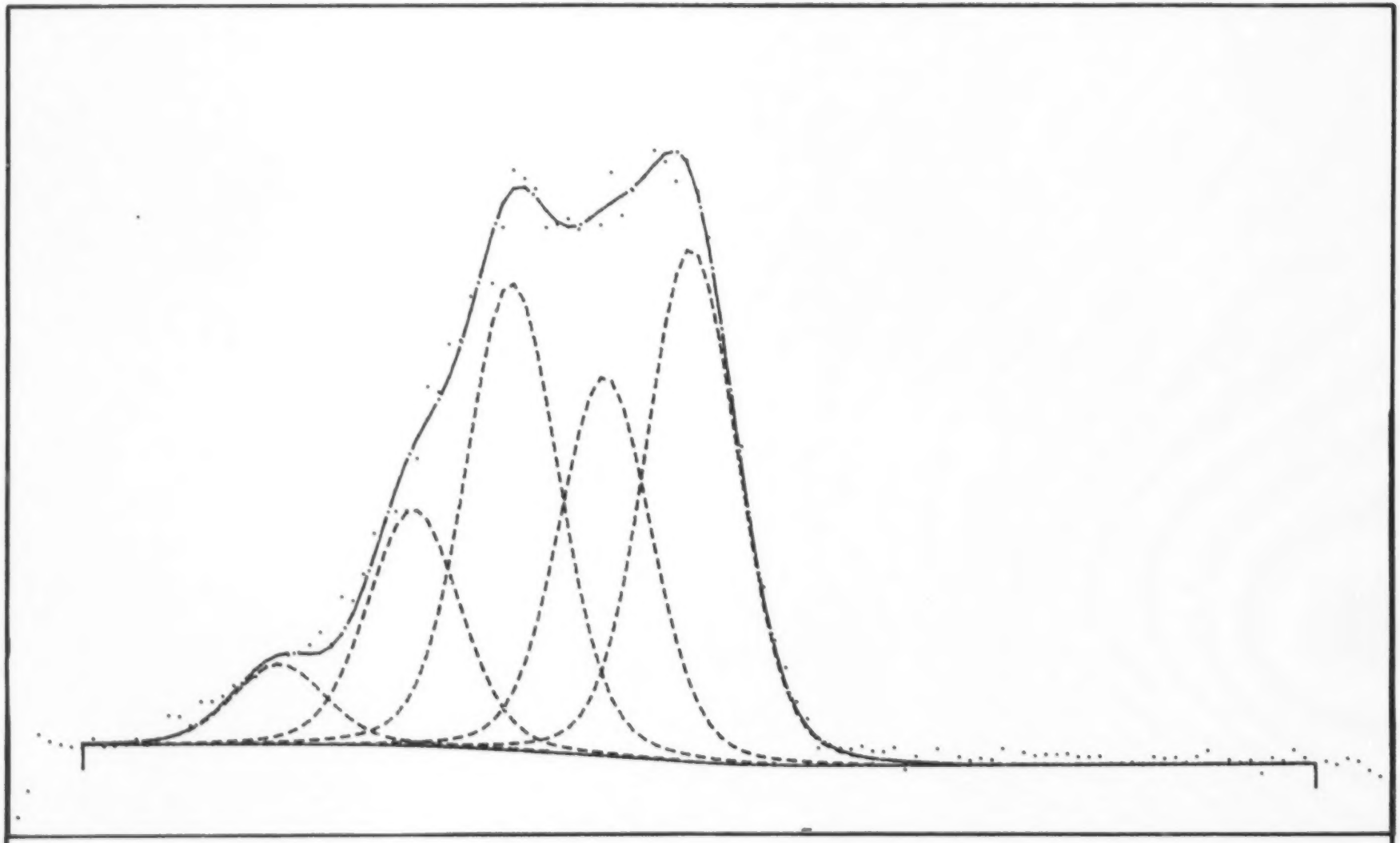
POSITIVE SECONDARY ION IMAGES FROM P-648 COAL TREATED SEQUENTIALLY WITH CD_3I, Ag^+ AND RbOH IMAGE DIAMETED IS 400μ, EXPOSURE TIMES ARE RECORDED WITH EACH IMAGE

Figure 13



XPS BROADSCAN OF P-807 TREATED WITH TOLLEN'S REAGENT

Figure 14



XPS SCAN OF CIS REGION OF P-807 TREATED WITH TOLLEN'S REAGENT